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## ENERGY & ENVIRONMENT DIVISION

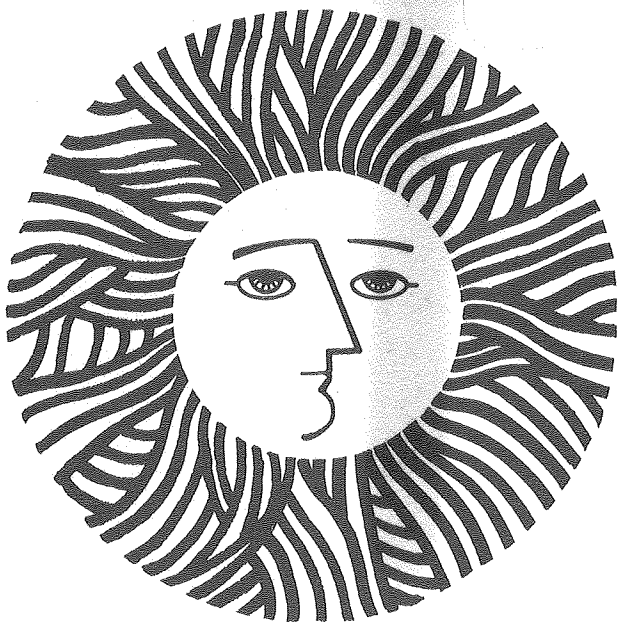
THE USE OF FERRIC SULFATE - ACID MEDIA FOR THE  
DESULFURIZATION OF MODEL COMPOUNDS OF COAL

Lloyd R. Clary\*, Theodore Vermeulen, and Scott Lynn  
(M.S. thesis)\*

December 1980

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THE USE OF FERRIC SULFATE - ACID MEDIA FOR THE DESULFURIZATION  
OF MODEL COMPOUNDS OF COAL

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ABSTRACT

The objective of this work has been to investigate the ability of ferric sulfate - acid leach systems to oxidize the sulfur in model compounds of coal. A coal desulfurization process which will operate at mild conditions, using an easily regenerable desulfurization agent, with little coal alteration, and recover sulfur in useable form, is highly desirable. A pre-combustion oxidative process which will remove organic sulfur has not been found. Ferric iron - acid leach systems have been shown to be quite effective at removal of inorganic sulfur in coal. In this study, the oxidative effect of ferric iron in acid-leach systems was studied using dibenzothiophene, diphenyl sulfide, and di-n-butyl sulfide as models of organic sulfur groups in coal. Nitrogen and oxygen, as well as various transition metal catalysts and oxidants, were utilized in this investigation.

Dibenzothiophene was found to be quite refractory to oxidation, except in the case where metavanadate was added, where it appears that 40% oxidation to sulfone could have occurred per hour at 150°C and mild oxygen pressure. Diphenyl sulfide was selectively

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oxidized to sulfoxide and sulfone in an iron and oxygen system. Approximately 15% conversion to sulfone occurred per hour under these conditions. Some of the di-n-butyl sulfide was cracked to 1-butene and 1-butanethiol under similar conditions.

Zinc chloride and ferric iron were used at 200°C in an attempt to desulfonate dibenzothiophene sulfone, diphenyl sulfone, and di-n-butyl sulfone. Di-n-butyl sulfone was completely desulfurized in one hour and fragmented to oxidized paraffins, while dibenzothiophene sulfone and diphenyl sulfone were unaffected.

These results suggest that an iron - acid leach process could only selectively oxidize aryl sulfides under mild conditions, representing only 20% of the organic sulfur in coal (8% of the total sulfur). Removal through desulfonation once selective sulfur oxidation had occurred was only demonstrated for alkyl sulfones, with severe oxidation of the fragmented paraffins also occurring in one hour.

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## I. INTRODUCTION

### A. Background

#### 1. Historical Perspective

With the Arab oil embargo and ever-increasing instability in the Persian Gulf region, the American government has come to realize that the United States must strive to become energy-independent. Since coal constitutes almost 90% of American fossil fuels that can be recovered with current technology, a rational long-term energy policy for our country must emphasize coal.

#### 2. Importance of Coal

With roughly 200-250 billion tons of "easily recoverable" coal, and each ton approximately equivalent to 3.75 bbl of crude oil, we possess twice the energy-content equivalent of the proven currently recoverable fossil fuel reserves of the Middle East. Indeed, the continental United States boasts roughly one-third of the world's known economically recoverable coal reserves.<sup>39</sup> Coal is abundant in the United States by almost any measure. In the unlikely event that all of the energy consumed in this country (approx. 100 quads/yr) were to be supplied by coal, the 21,000 to 36,000 quads of total estimated recoverable coal energy (1036-1788 billion tons) could supply all of our energy needs for several centuries. Estimates of the coal resources of the United States are given in Table 1.<sup>47</sup> Of course, nuclear fission reactors, oil, gas, and hydroelectric power sources will continue to contribute over the next several decades. Until breeder technology, fusion, or alternative energy sources are available, coal will have to supply a large portion of our needs. We

must strive to make this fuel resource environmentally acceptable and economically feasible.

Table 1. Estimates of fossil fuel resources ( after Wardworthy, ref. 47 ).

	<u>Proved and Currently Recoverable</u>		<u>U.S. % of World</u>	<u>Estimated Total Remaining Recoverable</u>		<u>U.S. % of World</u>
	<u>U.S.</u>	<u>World</u>		<u>U.S.</u>	<u>World</u>	
Crude Oil, 10 <sup>9</sup> bbl (quads) <sup>a</sup>	29.5 (171)	534-656 (3095-3800) <sup>b</sup>	5	144-371 (835-2154)	1430-2063 (8290-11970)	7-26
Natural Gas, 10 <sup>12</sup> cu ft (quads)	209 (213)	2226-2601 (2290-2680)	9	760-1170 (776-1195)	9000-9410 (9270-9690)	8-13
Natural Gas Liquids, 10 <sup>9</sup> bbl (quads)	6.0 (24)	62.2-71.5 (250-290)	9	21-33 (85-131)	252-263 (1000-1050)	8-13
Syncrude from Shale, Tar Sands, 10 <sup>9</sup> bbl (quads)	76.5 (444)	265 (1540)	29	1041 (6038)	2320 (13500)	45
Coal, 10 <sup>9</sup> tons (quads)	218 (4796)	732-787 (17400-18700) <sup>b</sup>	29	1036-1788 (20715-35753)	5544-6296 (126400-141500)	16-32
Total (quads)	(5648)	(24600-27000)	22	(28450-45270)	(158400-177700)	16-29

Footnotes: a. One quad = 10<sup>15</sup> BTU

b. These figures are corrected values.

The publisher's figures were low by an order of magnitude. With these corrections, the sum of column 2 is the author's total.

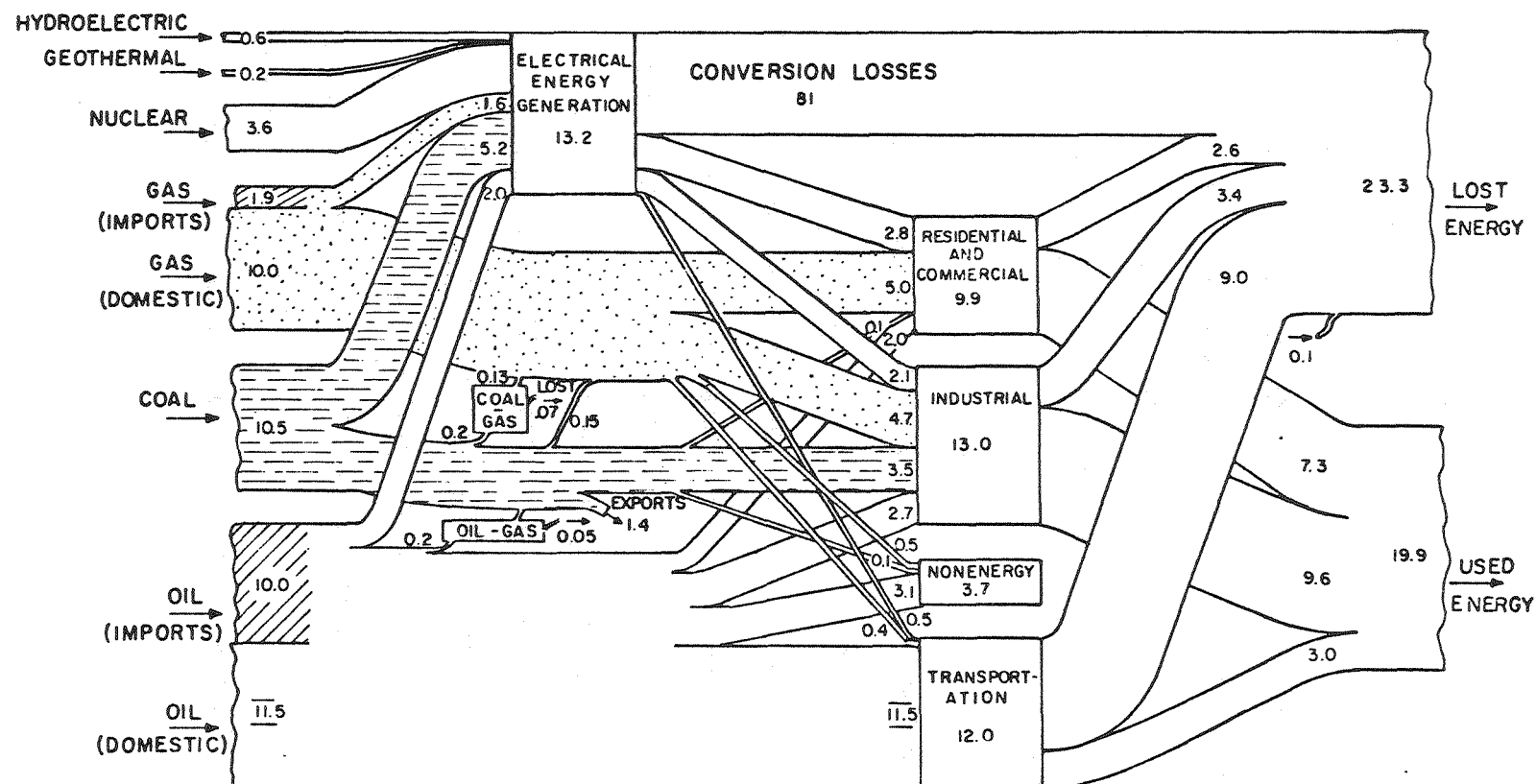
### 3. Current Coal Usage

Coal currently supplies one-fifth of our country's total energy demand, including one-half the electricity produced.<sup>34</sup> Last year we used 37.8 quads of petroleum and natural gas liquids, but produced only 20.7 quads. Expensive imports made up the difference.<sup>47</sup> To close this gap, power plants and industrial boilers using liquid fuels will have to switch to higher-sulfur domestic coal or coal-derived liquids. Coal will also have to be used extensively as feedstock for transportation fuels, home-heating oils, and chemical manufacture.

Of the current total United States usage of 100 quads/yr (48.3 MM<sup>\*</sup> bbl/day oil equivalent), we see from Figure 1 that coal can potentially replace 7.6 quad/yr (3.6 MM bbl/day) in utilities and 15.6 quad/yr (7.4 MM bbl/day) in industry. We see that simply converting our gas-burning and oil-burning utilities and industrial boilers to domestic coal will help greatly in eliminating our 25.1 quad/yr (11.9 MM bbl/day) of oil and gas imports. Indeed, this process is occurring at a rapid pace, especially since the government has recently restricted oil imports to 8.2 MM bbl/day.

Residential, commercial, transportation, and other oil and gas users who could switch to coal-derived fuels currently consume 43.3 quad/yr. Some of these heavy users of crude oil could potentially convert to coal feedstocks if coal could be liquefied (or gasified) or cleaned.

\* Throughout the text M=10<sup>3</sup>, MM=10<sup>6</sup>.



$\Sigma = 48.3$  MM BBLs/DAY OIL EQUIVALENT  
 = 100 QUADS/YEAR

NOTES: a. NUCLEAR SOURCES ARE LESS THAN 3.6 MM BBLs/DAY DUE TO HOLDUPS IN LICENSING.  
 b. OIL IMPORTS ARE CURRENTLY LIMITED TO 8.2 MM BBLs/DAY.

XBL 807-5409

Figure 1. United States Energy Usage (Approx. 100 quads/yr) in 1980  
 (after Austin, ref. 8).

#### 4. Environmental Hazards of Coal Combustion

The combustion of coal poses global hazards of increased atmospheric  $\text{CO}_2$  and particulates. In addition, burning of coal produces sulfur oxides, nitrogen oxides, and potentially carcinogenic polyaromatics in soot which pose extreme local health problems. The pollution and health hazard posed by these products is compounded, especially in the East, by stagnant weather (see Figure 2). This inability to disperse pollutants is even more severe when geographical "air basins" are present.

Point sources, such as power plants with tall stacks, can give  $\text{SO}_x$  a very long residence time in the atmosphere.<sup>40</sup> These highly concentrated pollutants may descend in localized urban areas, especially when the air is stagnant.

#### 5. Environmental Hazards Posed by $\text{SO}_2$

Sulfur dioxide alone is an irritant, but in high concentrations causes direct damage to human health. In addition,  $\text{SO}_x$  emissions can cause extensive agricultural damage, wildlife depletion, and corrosion of buildings.<sup>24</sup> Sulfur dioxide is especially dangerous in conjunction with other combustion products. Moisture, heavy metals, CO, NO, ozone, and particulates may compound the danger of  $\text{SO}_x$ . Comparing sides A. and B. of Figure 3, we see that plants exhibit leaf damage and reduced growth at  $\text{SO}_2$  concentrations where significant human health effects occur. Indeed, the animal and plant kingdoms appear to be about equally sensitive to  $\text{SO}_2$  over a wide range of concentrations.<sup>44</sup>

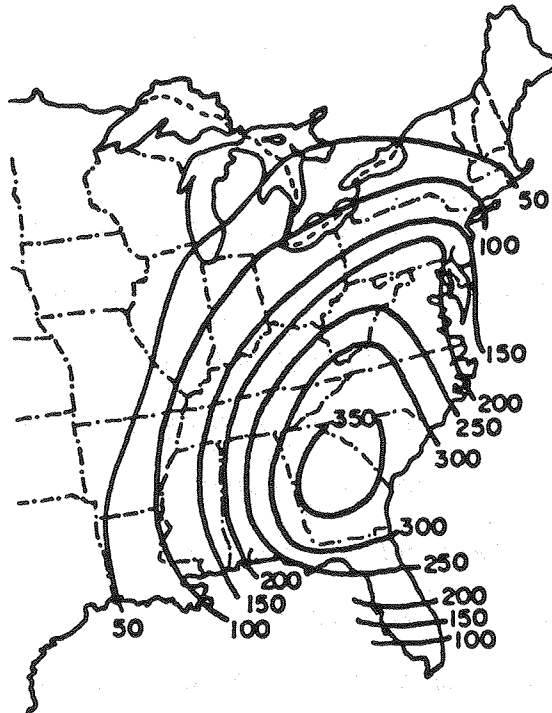
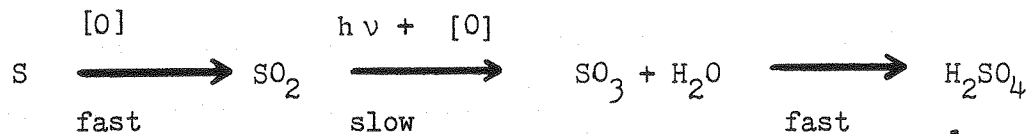


Figure 2. Days of Stagnant Weather, 30 Years of 1936-1965 (ref. 3).

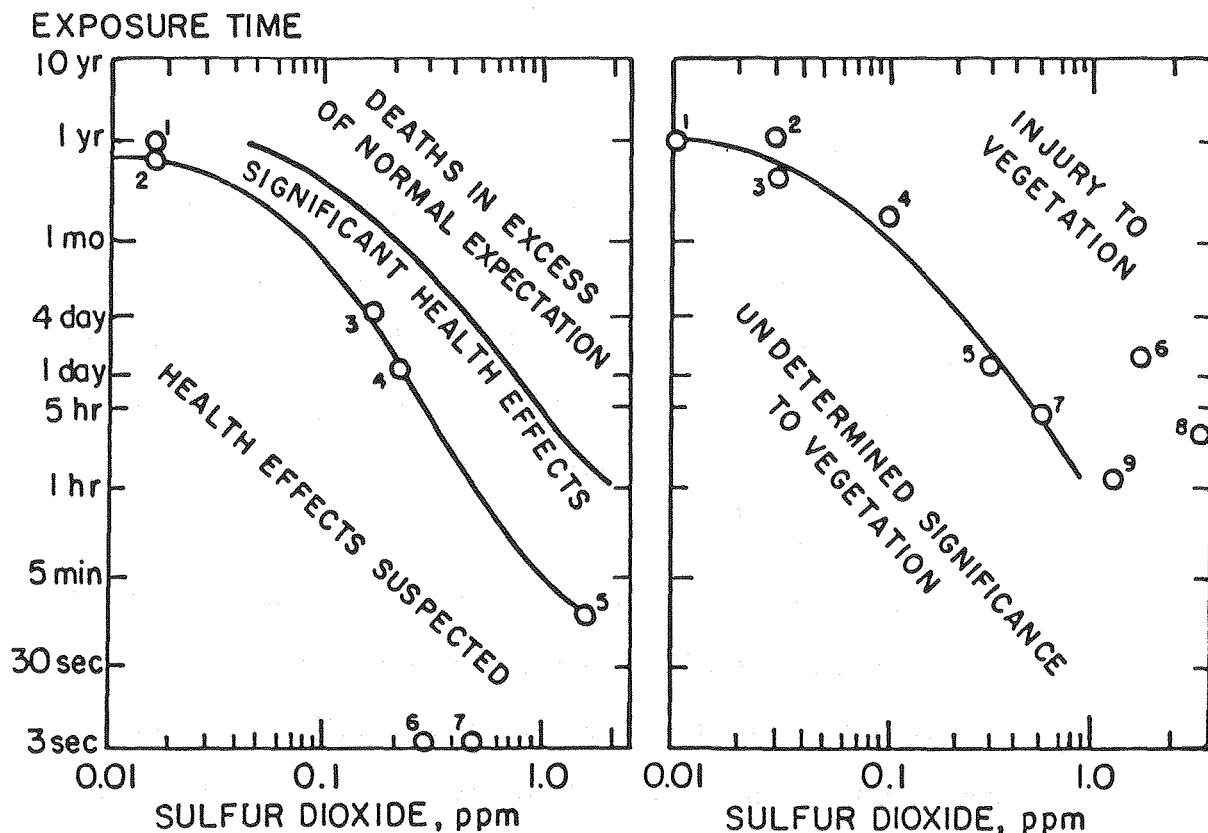
The source of  $\text{SO}_2$  is direct combustion of sulfur present in coal in the furnace. Sulfur dioxide is then slowly oxidized photochemically in the atmosphere, finally forming sulfuric acid or sulfates:<sup>4</sup>



Sulfuric acid and sulfur trioxide cause increased asthma frequency, cardio-pulmonary aggravation, decreased ventilation efficiency, and higher death rates.<sup>18</sup> These health effects are reviewed in Table 2. The sulfurous smogs of London, New York, and the Ruhr Valley in the 1950's and 1960's were attributed to



Figure 3. Effects of Sulfur Oxide Pollution (after Squires, ref. 44).



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A. Hazards to Human Health

- Key:
- 1 Increased cardiovascular morbidity
  - 2 Increased hospital admissions
  - 3 Increased incidence of cardiorespiratory disease
  - 4 Deterioration in health of bronchitis patients
  - 5 Increased airway resistance
  - 6 Taste threshold
  - 7 Odor threshold

B. Vegetable Destruction

- Key:
- 1 30% of gardens injured
  - 2 Growth retardation and chlorosis of white pine, 89% of gardens injured
  - 3 81% of pine trees without cones
  - 4 Premature abscission of older leaves of alfalfa
  - 5 Traces of leaf destruction in alfalfa
  - 6 50% leaf destruction in alfalfa
- See next page

<sup>7</sup>Acute injury to  
to leaves of trees  
and shrubs

<sup>8</sup>Same as item 6

<sup>9</sup>Same as item 5

high-sulfur coal combustion. These incidents resulted in widespread physical discomfort and increases in human mortality.<sup>44</sup>

Sulfuric acid, carried deep into the lungs on soot, causes permanent scarring. Carcinogens, such as benzo-(a)-pyrene and dibenzanthracene, may occur in fly-ash. Their danger may be promoted by SO<sub>2</sub>.<sup>17</sup>

Economic loss from SO<sub>2</sub> pollution includes crop, ecological, and materials damage. These losses may amount to an average of \$20/μg m<sup>-3</sup> yr (\$160 million/yr in the Northeast). The "acid rain" from H<sub>2</sub>SO<sub>4</sub> has severely reduced freshwater fish populations in some areas. The quantity of sulfate salts in rainwater, such as NH<sub>4</sub><sup>+</sup> and Pb<sup>+2</sup>, have increased dramatically in the Los Angeles area in recent years. High levels of sulfate, from 9 to 14 μg/m<sup>3</sup> in the atmosphere, have contributed to the disappearance of agriculture in the L.A. basin.

Obviously, the health effects of SO<sub>2</sub> are widespread and devastating. The proposed conversion to greater coal usage will have to consider control of additional SO<sub>2</sub> emissions. The government has attempted to define safe levels of SO<sub>2</sub> emissions from point sources to solve this problem.<sup>4</sup>

Table 2. Results of Epidemiological Studies (after Wrathall, ref. 52).

Adverse health effect	Concentration at which effect was observed <sup>a</sup>		Averaging time
	SO <sub>2</sub> μg/m <sup>3</sup> (ppm)	Atmospheric sulfate <sub>3</sub> μg/m <sup>3</sup>	
Increased mortality	300-400 (0.11-0.15)	NA <sup>b</sup>	24 hr
Aggravation of symptoms in elderly	365 (0.14)	8-10	24 hr
Aggravation of asthma	180-250 (0.07-0.09)	6-10	24 hr
Decreased lung function in children	220 (0.075)	11	Annual mean
Increased acute lower respiratory disease in families	90-100 (0.034-0.037)	9	Annual mean
Increased prevalence of chronic bronchitis	95 (0.035)	14	Annual mean
Increased acute respiratory disease in families	106 (0.039)	15	Annual mean
Increased respiratory disease related illness absences in female workers	—	13	Annual mean
EPA primary standard	365	-	24 hr
EPA primary standard	80	-	Annual mean

Footnotes: <sup>a</sup> Effects levels are best judgement estimates based on a synthesis of several studies

<sup>b</sup> NA = not available

6. Environmental Protection Agency Standards for SO<sub>2</sub>

The Environmental Protection Agency has agreed on ambient air quality standards which would appear to protect the environment.<sup>3</sup> National primary standards for SO<sub>2</sub> are 80  $\mu\text{g}/\text{m}^3$  (0.03 ppm) as an annual mean, and 365  $\mu\text{g}/\text{m}^3$  (0.14 ppm) as a maximum 24-hr concentration not to be exceeded more than once a year.<sup>1</sup>

Primary standards are based on protection of public health; secondary standards protect public welfare, including protection against the effects of air pollution on property, materials, climate, economic values, and personal comfort. These standards indicate ambient levels of pollution that cannot legally be exceeded in a specific geographical region.<sup>49</sup>

E.P.A. standards of performance for electric utility and industrial steam-generating units allow the following gaseous-effluent content of SO<sub>2</sub> for solid fuel or solid-derived fuel combustion:

- 1). 1.20 lb SO<sub>2</sub>/MM BTU heat input of solid fuel or solid-derived fuel and 90% reduction in potential combustion concentration of SO<sub>x</sub>,  
or
- 2). when uncontrolled emissions are less than 0.60 lb SO<sub>2</sub>/MM BTU heat input, 70% reduction of the potential combustion concentration is required.

For the combustion of liquid or gaseous non-coal derived fuels:

- 1). 0.80 lb SO<sub>2</sub>/MM BTU heat input and 90% reduction in potential concentration of SO<sub>x</sub>,  
or

- 2). when uncontrolled emissions are less than 0.20 lb SO<sub>2</sub>/MM BTU  
no reduction is required.<sup>1</sup>

For a moisture-free eastern coal (Illinois #6) at 5.0 wt-% sulfur, 8.3 lb SO<sub>2</sub>/MM BTU results. For a lignite western coal (Wyodak) with 0.8 wt-% sulfur, 2.0 lb SO<sub>2</sub>/MM BTU results.

Table 3. Calculation of SO<sub>2</sub> Production from  
Coal Combustion.<sup>52</sup>

Illinois #6 Coal	$\frac{0.05 \text{ lb S}}{1 \text{ lb coal}}$	$\times \frac{1 \text{ lb coal}}{12 \text{ MBTU}}$	$\times \frac{10^3 \text{ MBTU}}{\text{MM BTU}}$	$\times \frac{2 \text{ lb SO}_2}{1 \text{ lb S}}$	$= \frac{8.3 \text{ lb SO}_2}{\text{MM BTU}}$
Wyodak Coal	$\frac{0.008 \text{ lb S}}{1 \text{ lb coal}}$	$\times \frac{1 \text{ lb coal}}{8 \text{ MBTU}}$	$\times \frac{10^3 \text{ MBTU}}{\text{MM BTU}}$	$\times \frac{2 \text{ lb SO}_2}{1 \text{ lb S}}$	$= \frac{2.0 \text{ lb SO}_2}{\text{MM BTU}}$

Current E.P.A. standards would require that both of these coals receive 90% sulfur removal by cleaning, since uncontrolled SO<sub>2</sub> emissions are greater than 0.6 lb SO<sub>2</sub>/MM BTU. The E.P.A. standards, as written, discriminate against low-sulfur western coals. As the law now stands, all coals above 0.6 lb SO<sub>2</sub>/MM BTU potential emissions must have removal of 90% of the original sulfur. Such removal for Wyodak coal would yield a final value of 0.2 lb SO<sub>2</sub>/MM BTU while the same standard for Illinois #6 would yield 0.83 lb SO<sub>2</sub>/MM BTU as a final emission. Since typical flue gas desulfurization efficiencies are 85 to 95% at high concentrations, but are much more difficult at low concentrations of SO<sub>x</sub>, western coal clean-up is much more difficult.<sup>2</sup> Western coals with sulfur dioxide potential below 0.6 lb SO<sub>2</sub>/MM BTU will still be required to effect 70% removal. Many authors feel that the law will be changed so that 1.2 lb SO<sub>2</sub>/MM BTU will be a final requirement, with no percentage

removal required. If this is the case, western coals would only have to receive 40% sulfur removal; Illinois #6 would require 85% removal.

As a possible incentive to alternative desulfurization technologies, the E.P.A. has allowed combinations of physical/chemical cleaning,  $\text{SO}_4^{-2}$  fixation in slag or bottom ash, coal gasification or liquefaction as methods to achieve the 90% reduction required.

#### 7. Sulfur Dioxide Emissions in the United States

Coal combustion is the primary source of  $\text{SO}_2$  in the United States (see Table 4). Further conversion to this high-sulfur fuel will require additional pollution-control equipment or removal techniques to prevent an increase in ambient  $\text{SO}_2$  levels.

Table 4. Sulfur Dioxide Emission Sources, 1972.<sup>34</sup>

		MM ton/yr		%
Combustion of Coal	Utilities	16.5	} 19	58.1
	Industrial/ Commercial	2.5		
Combustion of Oil	Utilities	1.5	} 2.5	7.6
	Industrial/ Commercial	1.0		
Smelting/Industrial Processes		6.8	} 10.4	31.8
Area Industrial Sources		3.5		
Other Industrial		0.1		
Transportation	Auto	0.2	} 0.8	2.5
	Other	0.4		
Solid Waste		0.1		
Miscellaneous		0.1		
		<hr/>		
		$\Sigma = 32.7 \text{ MM tons } \text{SO}_2/\text{yr}$		

Table 5. Coal-fired Boilers of the U.S., 1972.<sup>34</sup>

Consuming Sector	No. of Units	Ave. Size MM BTU/hr	Annual Coal Consumption	MM ton/yr SO <sub>2</sub> uncleaned emissions
Utilities	1500	1000	9.31 quad	16.3 - 16.5
Industrial/Commercial	200,000	3.5 - 4.0	1.1 quad	1.8 - 2.5

Table 6. Oil-fired Boilers of the U.S., 1972.<sup>34</sup>

Consuming Sector	No. of Units	Ave. Size MM BTU/hr	Annual Oil Consumption	MM ton/yr SO <sub>2</sub> uncleaned emissions
Utilities	1000	700	2.59 quad	1.5
Industrial/Commercial	300,000 to 400,000	3.0 - 3.5	1.76 quad	1.0 - 1.3

Utility usage of coal and oil is increasing. The 1980 figure for utility coal use is 10.98 quad. In 1980 utility oil use is 4.22 quad, a sizable jump from 1972 usage. Converting this 4.22 quad to coal will add substantially to our uncleaned SO<sub>x</sub> emissions. Total 1980 industrial use in boilers, smelters, and other industrial processes is 7.39 quad for coal and 5.70 quad for oil. Obviously any conversion to coal in this area will also add substantially to overall SO<sub>x</sub> emissions. The total potential for oil-to-coal conversions is 9.92 quad. This would bring total coal use to 28.29 quad/yr. This is equivalent to an uncleaned emission level of 49.8 MM ton SO<sub>2</sub>/yr, a 52% increase over current levels.

Small industrial users converting to coal are struggling to meet the high capital costs for scrubbers. A coal-cleaning technique accomplished at the mine would help them considerably. Utility and industrial users would also prefer pre-combustion cleaning so that they can avoid large operating costs, corrosion,

and solid waste disposal problems posed by existing flue-gas desulfurizers.

### 8. Forms of Sulfur in Coal

Desulfurization processes are dependent on the nature of sulfur in coal. Sulfur appears in both organic and inorganic forms. Total sulfur in coal can range from 0.2 to 10.0 wt-%, but usually ranges from 1 to 4 wt-%.<sup>5</sup> The ratio of inorganic to organic sulfur ranges from 1:3 to 4:1 but usually is between 1:1 and 2:1 ; inorganic sulfur is therefore usually 50 to 70% of the total.

Inorganic sulfur is composed of pyrite ( $\text{FeS}_2$ ), pyrrhotite ( $\text{FeS}$ ), sulfates, and elemental sulfur in that order of abundance. Pyrite is usually overwhelmingly predominant, with trace amounts of the others. Galena ( $\text{PbS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), and Sphalerite ( $\text{ZnS}$ ) are sometimes present. Sulfates, in the form of iron, calcium, and barium salts, are usually found only in weathered coals. Table 7 gives distribution of sulfur in some average United States coals. We see that inorganic sulfur ranges from 50 to 70% of the total in these representative samples.

Table 7. Distribution of Sulfur in U.S. Coals.

Sample (ref. 33)	Sulfur (%)				Ash (%)
	Total	Pyritic	Sulfate	Organic	
719-2 (Ohio)	6.3	1.58	2.74	1.9	14.2
719-3 (Ohio)	5.2	3.6	0.07	1.4	17.1
Hazard #4 (Kentucky)	1.52	0.66	0.04	0.82	12.8
Colstrip #2 (Western)	0.68	0.18	0.14	0.36	9.0
Beach Bottom #1 (W.Va.)	1.97	1.35	0.03	0.59	25.1



Coal (ref. 32)	Total S	Inorganic S	Organic S	Ash (%)
Indiana V (Warrick Co.)	4.63	2.44	2.19	12.8
Indiana VI (Warrick Co.)	4.17	2.20	1.97	11.4
Illinois V (Wabash Co.)	3.59	2.39	1.20	10.3
Illinois VI (Williamson Co.)	1.98	1.02	0.96	7.1

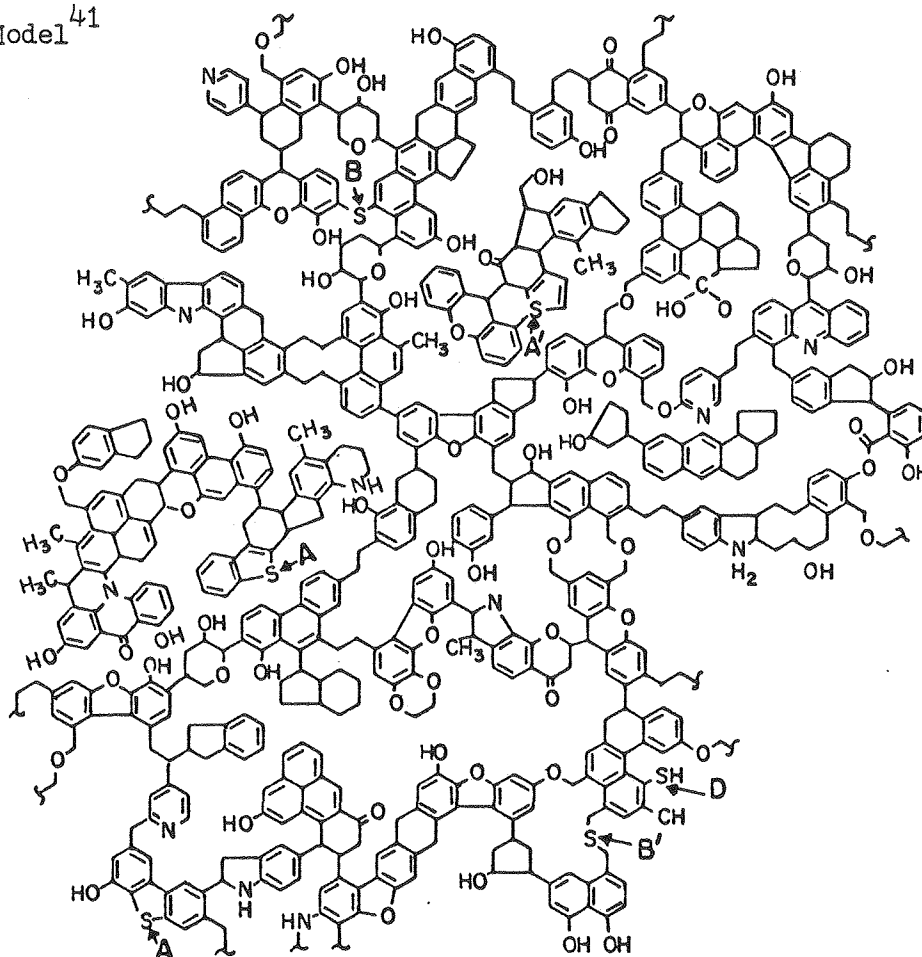
The organic sulfur is bound to the hydrocarbon structure of the coal. This organic sulfur is roughly distributed as follows in bituminous coals (higher ranked coals may have more condensed thiophenes)<sup>7</sup>:

Structure in Fig. 4

30% Condensed thiophenic	A
20% Thiophenic	A'
18% Aryl sulfide (Ar-S-Ar)	B
18% Aliphatic and Alicyclic sulfides (R-S-R)	B'
7% Disulfides (-S-S-)	C
7% Thiols (-SH)	D

See Figure 4 for illustrations of these structural groups as they occur in coal. Coal has a very complex structure, neither of the illustrations in Figure 4 are intended as exact representations.

A. Shinn Model<sup>41</sup>



B. Wiser Model<sup>50</sup>

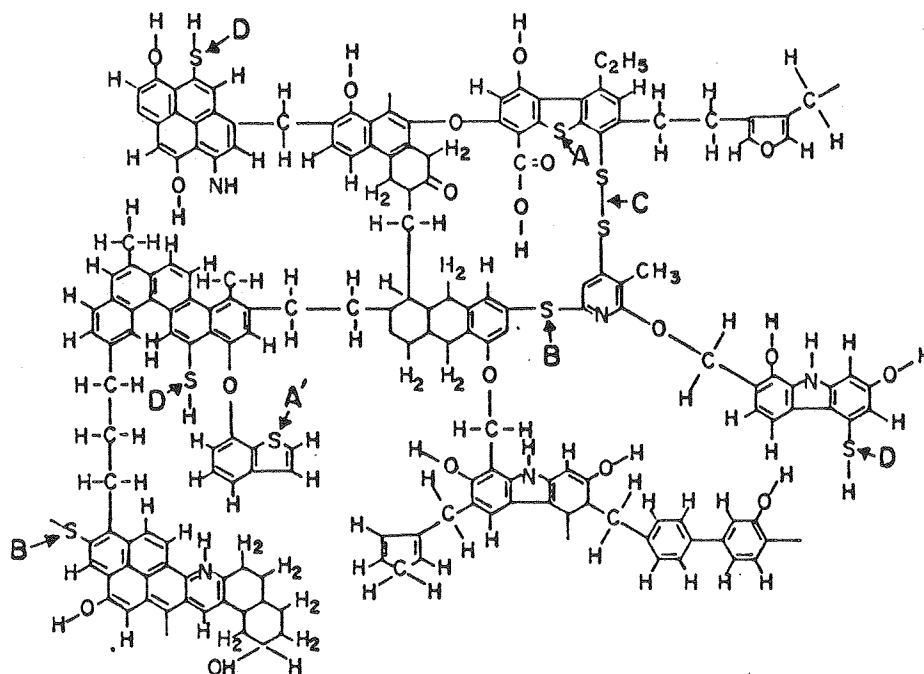


Figure 4. Representation of Functional Groups in Coal. XBL 807-5420

## 9. Sulfur Removal Techniques

Coal can be desulfurized prior to, during, or after combustion. Desulfurization prior to combustion can be divided into three categories: physical removal, extraction and leaching, and gas-solid reaction. Desulfurization during combustion involves sulfate fixation in ash or slag. Post-combustion desulfurization is also known as flue-gas scrubbing. Since this thesis is concerned with precombustion cleaning, only these methods will be reviewed.

### a. Physical Processes

Physical cleaning methods are used to remove pyrite. Pyrite has physical properties different from those of the organic material in coal. Density, wettability, or para-magnetic differences are used to effect separation. These methods, at best, can remove about 50% of the sulfur in coals. Such physical treatment may be advisable as a first step in treating coals.

Table 8. Physical Coal Cleaning Process Efficiencies.

<u>Method</u>	<u>Pyrite Removal Achieved</u>
Oil Agglomeration	30 - 60 %
Froth Flotation	50 - 75
Gravity Separation	50 - 75
Grinding	60 - 70
Chemical Communion	55 - 70
Dry Table	60 - 75
Magnetic Desulfurization	50 - 80

With roughly 60% of total sulfur as inorganics in most coals, and average removal efficiencies of 70%, we see that physical methods can potentially remove about 42% of total sulfur. This is all that would be required for the western coals to reach 1.2 lb SO<sub>2</sub>/MM BTU.

If the 90% removal clause is discarded in the present law, many western coals will be cleanable by physical methods.

b. Chemical Coal Cleaning

These processes involve extraction and leaching methods which are very good at removing pyrites and breaking weak organic-sulfur bonds. Some of the thiols and sulfides may be removable by these methods, but thiophenes are generally unaffected.

Table 9. Coal Cleaning Processes.

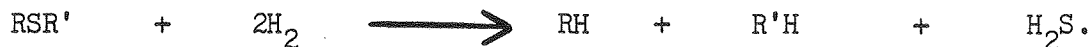
Process:	HAZEN	KVB	BATTELLE	TRW/ MEYERS	LEDGEMONT	BOM/ERDA
Method:	Dry Chemi- cal pretreat + magnetic separation	Dry ox- idation + caus- tic wash	Caustic leach	Acid leach	Oxygen leach	Air leach
Reagent:	Fe(CO) <sub>5</sub>	O <sub>2</sub> , N <sub>2</sub> , NO, H <sub>2</sub> O, NaOH	NaOH, Ca(OH), H <sub>2</sub> O, CO <sub>2</sub>	Fe(SO <sub>4</sub> ) <sub>3</sub> , H <sub>2</sub> O, O <sub>2</sub> , Tol- uene	O <sub>2</sub> , H <sub>2</sub> O, Lime	Air, H <sub>2</sub> O, Lime
Pressure: (psia)	40	35	570	15-80	315	1000
Retention: (hrs)	$\frac{1}{2}$	1	$\frac{1}{4}$	$\frac{1}{2}$ -10	2	1
Removal of Ash %:	40	-	-	-	-	-
Removal of Pyritics %:	100	100	100	100	100	100
Removal of organic S %:	0	40	25	0	0	40
Sulfur						
Product:	Dry sul- furous mineral matter	Gypsum	H <sub>2</sub> S, S	Iron sulfates, S	Gypsum	Gypsum

We see that the best organic removal claimed is 40% by these methods, with total pyritic removal possible in all cases. Since coal sulfur is roughly 60% inorganic, 20% "simple" organic (sulfides, thiols), and 20% "refractory" organics (thiophenes), this would indicate that the "simple" organic sulfur is substantially removable by leaching technology. Current chemical methods can therefore provide roughly 76% removal of total sulfur at best. Even with total inorganic and "simple" organic removal, we would still fall short of the 85% removal needed for our Illinois #6 coal. On the other hand, these methods will allow many coals to be cleaned successfully (those below 5.0 lb SO<sub>2</sub>/MM BTU or about 3.0 wt-% S.).<sup>23,37,45</sup>

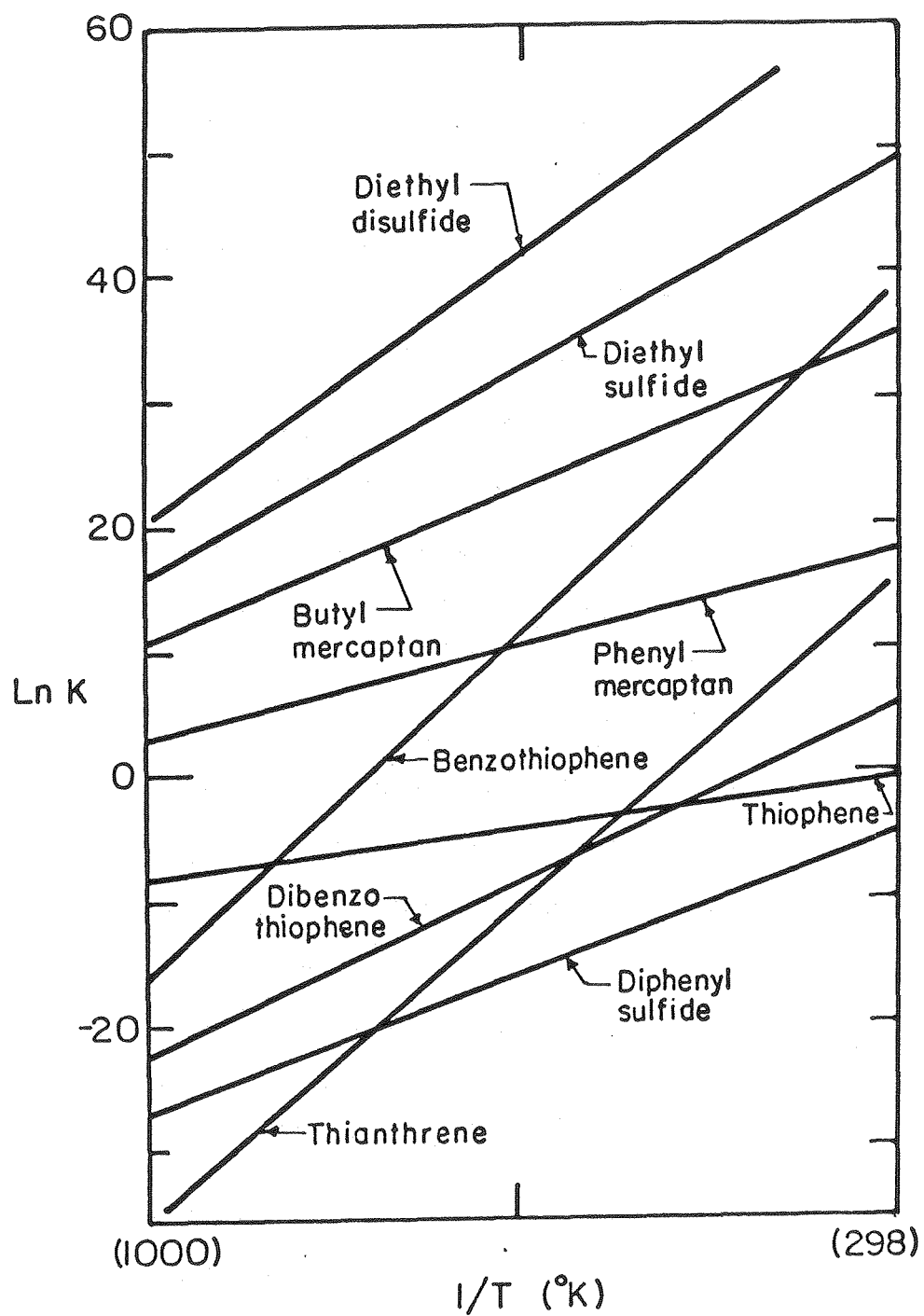
### c. Gas-Solid Reactions

These reactions are generally associated with hydrogenation and pyrolysis at high temperatures, as in coal conversion processes. Many new gas oxidation methods are being studied which are aimed at organic sulfur removal.

Hydrodesulfurization is one method which simply reacts hydrogen with organic sulfur as follows:



The H<sub>2</sub>S is treated conventionally to form elemental sulfur. These desulfurization reactions are generally highly exothermic at room temperature, so that equilibrium constants become less favorable at higher temperature. Figure 5 shows the equilibrium constants for benzothiophene, dibenzothiophene, diphenyl sulfide, thianthrene, thiophene, and several aliphatic sulfides versus



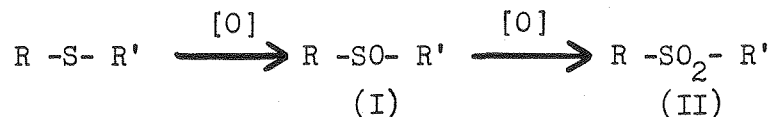
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Figure 5. Hydrodesulfurization Thermodynamics of Coal Model Compounds (ref. 52).

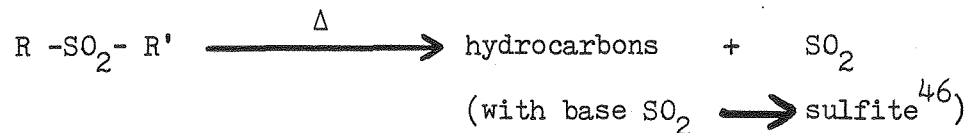
temperature. These values were calculated from thermodynamic data.

The rate is limiting in desulfurization reactions<sup>20</sup>, and can be increased substantially by higher temperature. In coal, hydrogenation of carbon-carbon bonds is an important competing reaction with similar kinetics. In condensed thiophenes and aromatic sulfides, the  $n$  electrons of the sulfur can resonate with  $\pi$  electrons of the aromatic rings<sup>13</sup>. This causes high Activation Energies so that desulfurization rate problems are more severe. In coal most carbon atoms are unsaturated<sup>48</sup>, and most organic sulfur is condensed thiophenic or aromatic, so that selective hydrodesulfurization has little success<sup>6</sup>.

Due to the difficulty of hydrodesulfurization, the aromatic and thiophenic sulfides are commonly called "refractory". Roughly 27% of the total sulfur (67.5% of the organic sulfur) is refractory. For this reason, 30 to 40% is probably the upper limit for removal of organic sulfur from coal by hydrogenation. Since we need to remove the roughly 60% of refractory organic sulfur in the total organic sulfur, oxidation methods are being considered as an alternative to hydrogenation. In "selective oxidation" methods, organic sulfur is oxidized to sulfoxides (I) and sulfones (II)<sup>21</sup>:

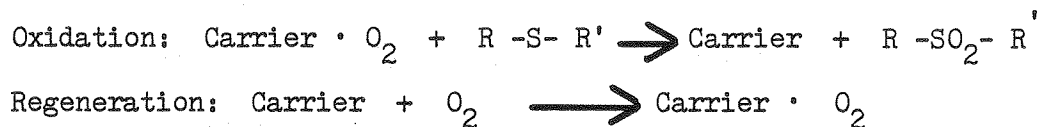


The sulfone product is thermally decomposed with or without base:

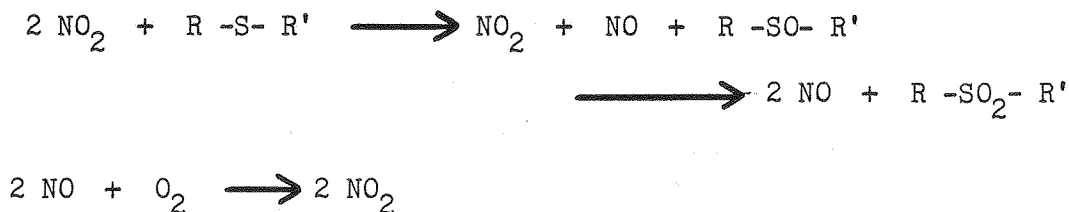


If R is aliphatic, an olefin is obtained<sup>12</sup>; if R is thiophenic or aromatic, phenols are obtained in the solution<sup>26</sup>. Oxidation of the sulfur reduces the C-S bond energy by 5.2 kcal/mole for aliphatics and 11.8 kcal/mole for aromatic and thiophenic sulfides. This dramatically increases the selectivity for breaking C-S bonds so that sulfur can be removed from the coal matrix<sup>11</sup>.

Oxidation should be rapid and selective, thus two basic methods have been considered. The first is direct molecular oxidation using O<sub>2</sub> or air. This is usually only effective in oxidizing thiols, and is carried out in basic solution. The second method is "indirect" oxidation using a regenerable oxygen carrier as below:

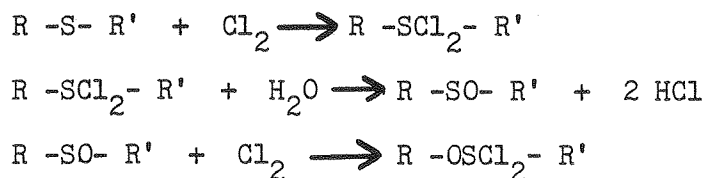


Several regenerable oxidizers have been investigated. Nitrogen dioxide has been shown, for instance, to oxidize 70% of the total sulfur at 140°C:



Nitrogen fixation and coal powder explosions are problems.

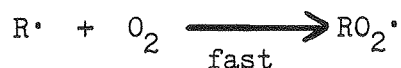
Chlorine, though not selective or regenerable, is another possibility:



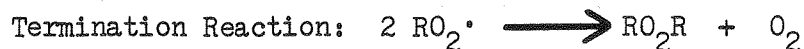




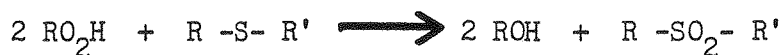
Though not regenerable, peroxidic species made from solvents can also selectively oxidize sulfur compounds.<sup>43</sup> The solvent is oxidized to form reactive hydroperoxides or peroxy acids, which then oxidize the sulfur.



(HO·, RO<sub>2</sub>·, and RO· are selective free radicals)



By a free-radical mechanism<sup>25</sup>, these oxidized solvents can oxidize coal sulfur:



Even if this method of "in situ" oxidation were absolutely selective, two hydrogens would be oxidized to hydroxy groups for each sulfone formed. Adding peroxidic decomposition without oxidizing sulfur makes this process less than 50% selective.<sup>6</sup>

#### 10. Applicability of Cleaning Processes to U.S. Coals

Since current coal cleaning removes only part of the total sulfur, we need to find out exactly what fraction of coals can be cleaned to meet current or proposed E.P.A. standards. A number of studies show that a great many coals can currently be cleaned to 1.2 lb SO<sub>2</sub>/MM BTU.

A report by Hamersma on the basis of 35 coals, showed that 40% of the samples could be burned cleanly after some combination of physical separation and chemical leaching<sup>22</sup>. A report by Ergun on coal cleaning gives a higher estimate on cleanability of 56%, based on 455 samples of eastern and western coals<sup>15</sup>. Ergun estimates an additional 17% is cleanable if 30 to 40% of the organic sulfur (non-refractory) is removed, bringing the total cleanable to 73%.

This means that some method of treating the 50 to 70% refractory fraction of the total organic sulfur must be found, if we are to clean the remaining 27% high sulfur coals prior to combustion.

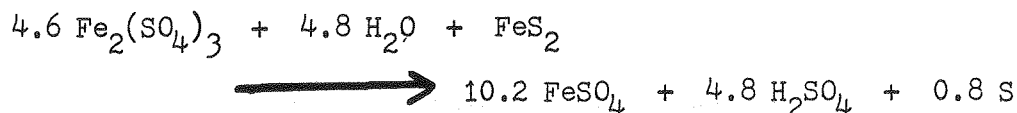
In summary, total inorganic removal would clean 40% of our coal. Cleanable coal increases another 33% if we can remove the more reactive organic sulfur species such as aliphatic mercaptans, sulfides, and disulfides<sup>27</sup>. A process that could remove refractory thiophenic sulfur would make the remaining 20 to 30% of our coal reserves accessible if there were an equal distribution between reactive and refractory organic sulfur<sup>52</sup>.

#### B. Purpose

The objective of this study was to examine the chemistry of refractory and relatively reactive organic sulfur species to a combination oxidation/chemical leaching process. An inexpensive method of pre-treating coal to remove refractory organic sulfur is desirable, but at present is not available. The best existing technology can only attack the relatively reactive organic sulfur groups. Examining the chemistry of refractory and reactive organic species may lead to a suitable coal cleaning process<sup>52</sup>.

### C. Scope

The research reported in this thesis is concerned primarily with investigating the potential effect of transition metals on organic sulfur model compounds in acid leach-water solutions. Meyers showed that aqueous oxidation of coal removes 85% of the inorganic sulfur with an aqueous solution of 5.0 wt-% ferric iron:<sup>28-30</sup>



Mixon and Vermeulen used aqueous solutions of  $\text{H}_2\text{SO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  to oxidize pyrite, in order to avoid formation of elemental sulfur and to recover  $\text{H}_2\text{SO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  as valuable by-products<sup>31</sup>. They found 90% removal of pyrite from Illinois #6 bituminous coal at 150 - 180°C and 400 psia  $\text{O}_2$  for 1 hr. These authors felt that addition of catalysts or supplementary reactants might result in substantial conversion of organic sulfur. They used 25%  $\text{H}_2\text{SO}_4$  and 12 - 15%  $\text{Fe}_2(\text{SO}_4)_3$  relative to  $(\text{H}_2\text{O} + \text{H}_2\text{SO}_4)$  content.

### D. Limitations

This research was limited to investigations of the reactions of three model compounds representative of three types of coal sulfur groups, with ferric sulfate and sulfuric acid at various concentrations. Various catalysts and inorganic oxidants were also added. No peroxides or gaseous oxidants other than molecular oxygen were used.

For studies of sulfone decomposition, only  $\text{ZnCl}_2$  in a ferric solution was studied.

## II. EXPERIMENTAL SECTION

### A. Chemical Selection

Three model compounds for organic sulfur in coal were selected. Dibenzothiophene is a very stable compound which models many condensed thiophenes in coal. Diphenyl sulfide was selected as a model of sulfide bridges between coal aromatic groups. Di-n-butyl-sulfide was selected as a model of simple alkyl sulfides in coal.

Ferric sulfate was selected as a possible oxidant or oxygen transfer species for attacking the model compounds. Zinc, manganese, and copper were chosen as possible catalytic ions<sup>10</sup>. Vanadium was selected as an additional strong oxidant.

Experiments were conducted under relatively mild conditions of temperature and pressure, and at sulfuric acid concentrations necessary to keep ferric iron dissolved.

### B. Materials Used

Chemicals which were used in the experiments are listed below. Four categories are given in Table 10. Model compounds of the coal sulfur groups are given first. These are followed by inorganic reactants and catalysts, analytical chemicals, and miscellaneous chemicals.

Table 10. Experimental Chemicals

	<u>Purity</u>	<u>Source</u>
1. Organic Model Compounds		
Dibenzothiophene	95%	Aldrich
Dibenzothiophene Sulfone	-	"
Phenyl Sulfide (Diphenyl Sulfide)	Gold Label 99 <sup>+</sup> %	"

	<u>Purity</u>	<u>Source</u>
Phenyl Sulfone	97%	Aldrich
n-Butyl Sulfide (Di-n-Butyl Sulfide)	97%	"
n-Butyl Sulfone	-	"
2. Inorganic Reactants and Catalysts		
Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ )	Analytical Reagent	Mallinckrodt
Ferric Chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )	"	"
Manganese Sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ )	"	"
Cupric Sulfate ( $\text{CuSO}_4$ )	"	"
Zinc Sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ )	"	"
Sulfuric Acid ( $\text{H}_2\text{SO}_4$ )	95-98%	"
Ammonium Metavanadate ( $\text{NH}_4\text{VO}_3$ )	-	City Chem Corp (NYC)
Zinc Chloride ( $\text{ZnCl}_2$ )	An. Reag.	Matheson, Coleman, & Bell
3. Analytical Chemicals		
Potassium Dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )	An. Reag.	Mallinckrodt
Hydrochloric Acid ( $\text{HCl}$ )	37%	"
Phosphoric Acid ( $\text{H}_3\text{PO}_4$ )	85%	"
Barium Chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ )	An. Reag.	"
Ferrous Sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )	"	"
Barium Diphenylaminesulfonate	Reagent	D. T. Baker
Sodium Sulfate ( $\text{Na}_2\text{SO}_4$ )	"	Matheson, Coleman, & Bell
Mercuric Chloride ( $\text{HgCl}_2$ )	"	Baker & Adamson
4. Miscellaneous		
Calcium Sulfate ( $\text{CaSO}_4$ ) Dessicant	-	Hammond Drierite
Mineral Oil (Nujol)	-	Plough
Acetone	An. Reag.	Mallinckrodt
Ethyl Ether	"	"

### C. Apparatus

A Monel bomb of 600 ml total volume, manufactured by Parr Instruments, was used in all experiments. This reactor was fitted with 304 and 316 stainless steel internals and a sleeve-type glass liner. The bomb was rated for high pressure ( $2000^+$  psia), but was fitted with a 1000 psia rupture disc. Temperature was monitored with an iron-constantan thermocouple, and was controlled with an 800-watt heating mantle and an internal cooling coil. Reactants were stirred with impellers mounted on a rotating shaft. A Teflon gasket was used to provide airtight sealing of the flanged reactor lid. Sealing rings and packing cones were used to seal the stirring shaft. The shaft seal and bearing area was jacketed and water cooled. Teflon splash guards were fitted inside and above the glass liner to prevent acid splash onto corrodable bomb material. An illustration of the apparatus is given in Figure 6.

### D. Procedure

Liquid and solid reactants were batch-loaded into the glass liner. Sulfuric acid and water were mixed in quantities depending on the desired acidity of the run. Ferric sulfate was added in quantities approaching fifty-percent of saturation at run temperature. Figure 7 shows ferric sulfate solubility in acid/water systems<sup>35</sup>.

Organic sulfides and when appropriate catalysts were then added to the aqueous mixture. The glass liner was placed in the bomb, and the apparatus was sealed. For zinc chloride desulfonation experiments, no acid or ferric sulfate was used. The solid in-

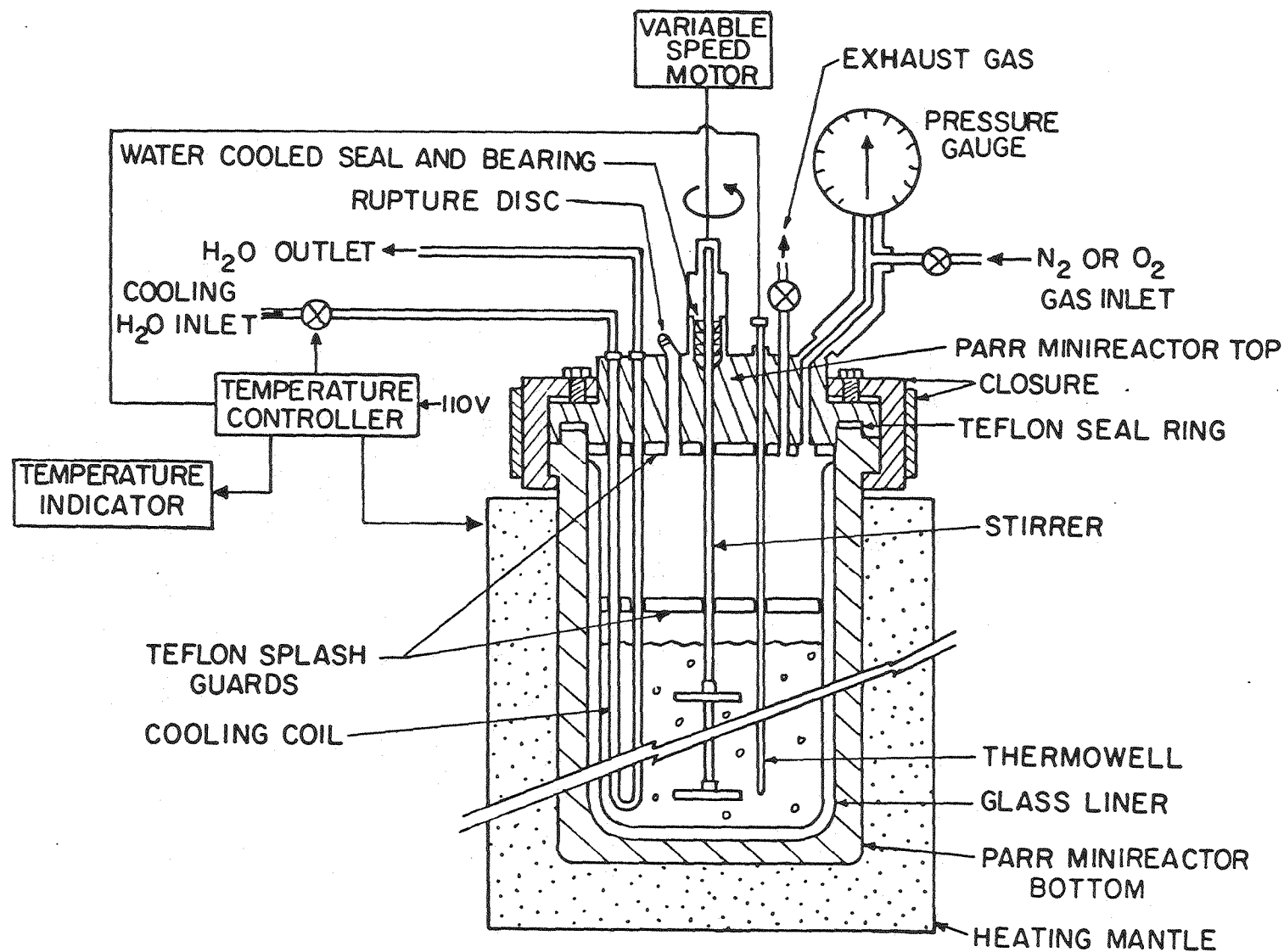


Figure 6. Apparatus for Coal Model Compound Experiments.

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organic reactants were preheated to melting to allow closure of the bomb, solid sulfones were added, and the bomb was sealed.

In all cases the atmosphere above the reactant mixture was flushed for five minutes with either oxygen or nitrogen, final cold pressure was set, then the system was sealed. The mixture was then heated to reaction temperature and maintained there for the duration of the run. Internal cooling was performed at the end of a run until room temperature was reached. The bomb was then dismantled and the products and any unreacted reactants were separated from the aqueous mixture. These organics were then analyzed for evidence of reaction.

For dibenzothiophene (solid at room T), the aqueous mixture was filtered at the end of a run. The solids were washed with acetone and filtered to remove inorganics. Acetone-soluble organics were recovered by distillation. These solids were then water-rinsed and dried in an oven. The solids were analyzed for evidence of oxidation. The aqueous filtrate was quantitatively analyzed for iron, then mixed with ether. After separation, the ether was distilled to check for liquid organics.

For Diphenyl sulfide and Di-n-butyl sulfide (liquids at room T), the aqueous mixture was filtered to remove inorganics. The aqueous mixture was analyzed for iron. Filtered solids and any organic liquids left on the filter were ether-washed and mixed with the aqueous phase. The ether and aqueous phases were well mixed to extract organics. After separation, the ether phase was rinsed with water to remove the acid, and was then slowly distilled. Any ether-extractable organics remaining after the



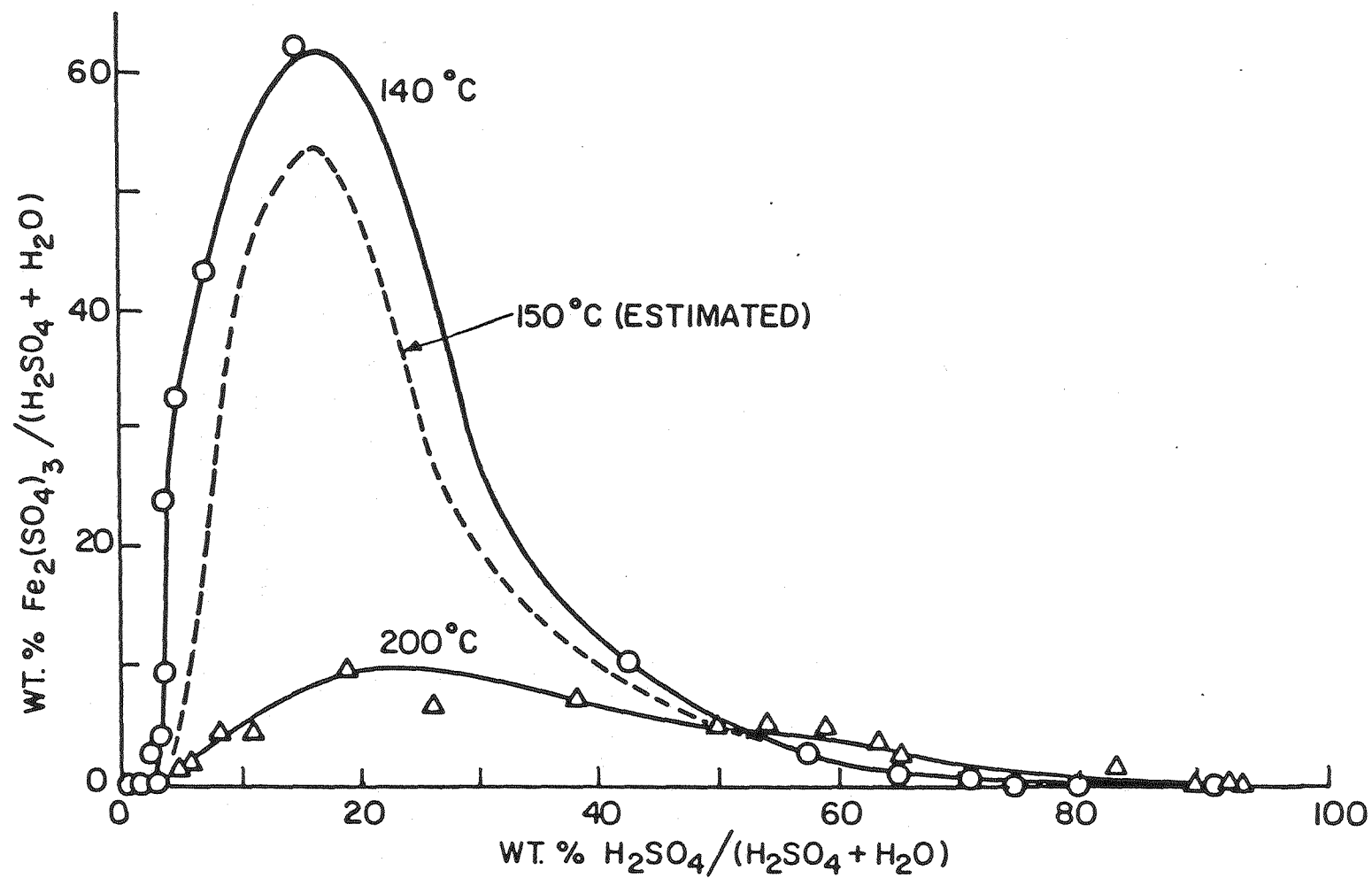


Figure 7. Ferric Sulfate Solubility in Acid Media (after Posnjak, ref. 35).

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distillation were dried with dessicant and analyzed.

For zinc chloride/sulfone experiments (sulfones are solid at room T), after the run, the zinc chloride slurry was diluted with water and filtered. The filtered solids were rinsed with acetone to dissolve them, then washed away from the inorganic residue. The acetone solubles in the filtrate were distilled, water-rinsed, and dried in the oven. These solids were analyzed for evidence of oxidation. Some of the aqueous filtrate from the initial separation was ether-rinsed and distilled to check for water-soluble or liquid organics. The remainder of the aqueous phase was analyzed for sulfate precipitates by adding barium chloride.

#### E. Analytical Methods

##### 1. Sulfur Analysis

Solids and liquids were analyzed by combustion in a furnace at  $850^{\circ}\text{C}$  with an oxygen flow of 10 ml/min, at atmospheric pressure, for a residence time of fifteen minutes. The sample size was 5 to 15 mg. The resultant  $\text{SO}_2$  was oxidized to  $\text{H}_2\text{SO}_4$  by  $\text{H}_2\text{O}_2$ , and precipitated with acidic  $\text{BaCl}_2$ . The resulting  $\text{BaSO}_4$  was filtered, dried, and weighed. In cases where sulfur remained in the residue, the residue was washed with HCl and precipitated as above.

##### 2. C-H Analysis

These analyses were made using a Perkin-Elmer 240 C-H-N analyzer. Combustion occurred at  $950^{\circ}\text{C}$  in a large excess of oxygen. Water and carbon dioxide produced were measured by a thermal con-

ductivity detector.

### 3. Iron Analysis

#### a. Total Iron

Total iron in a sample was determined by using a Perkin-Elmer 360 Atomic Absorption Spectrophotometer. The sample was digested in  $\text{H}_2\text{SO}_4$ , cooled, and  $\text{H}_2\text{O}_2$  was added to eliminate carbon formed from any organics. The resultant iron in the aqueous solution was run through the atomic absorption apparatus.

Alternatively, total iron was determined by reducing all the iron to  $\text{Fe}^{++}$ . One ml of aqueous solution was added to 20 ml of 6N HCl, heated to boiling and 0.26 M  $\text{SnCl}_2$  was added dropwise until a clear solution resulted. Two additional drops were added, then the mixture was cooled and 10 ml of  $\text{HgCl}_2$  solution was added to remove excess tin (II) which interferes with the iron analysis<sup>19</sup>. After three minutes this mixture was titrated for total iron, using  $\text{Cr}_2\text{O}_7^{=}$  as an oxidant as described below.

#### b. $\text{Fe}^{++}$ Determination

Ferrous iron concentration was obtained by titrating with standard potassium dichromate. Diphenylaminesulfonate was used as an indicator. Ordinarily this indicator changes color at too low a potential. For this reason, phosphoric and sulfuric acids were added to complex  $\text{Fe}^{+3}$  so that color change to violet occurred at the end point of the titration. This effect is shown in Figure 8.

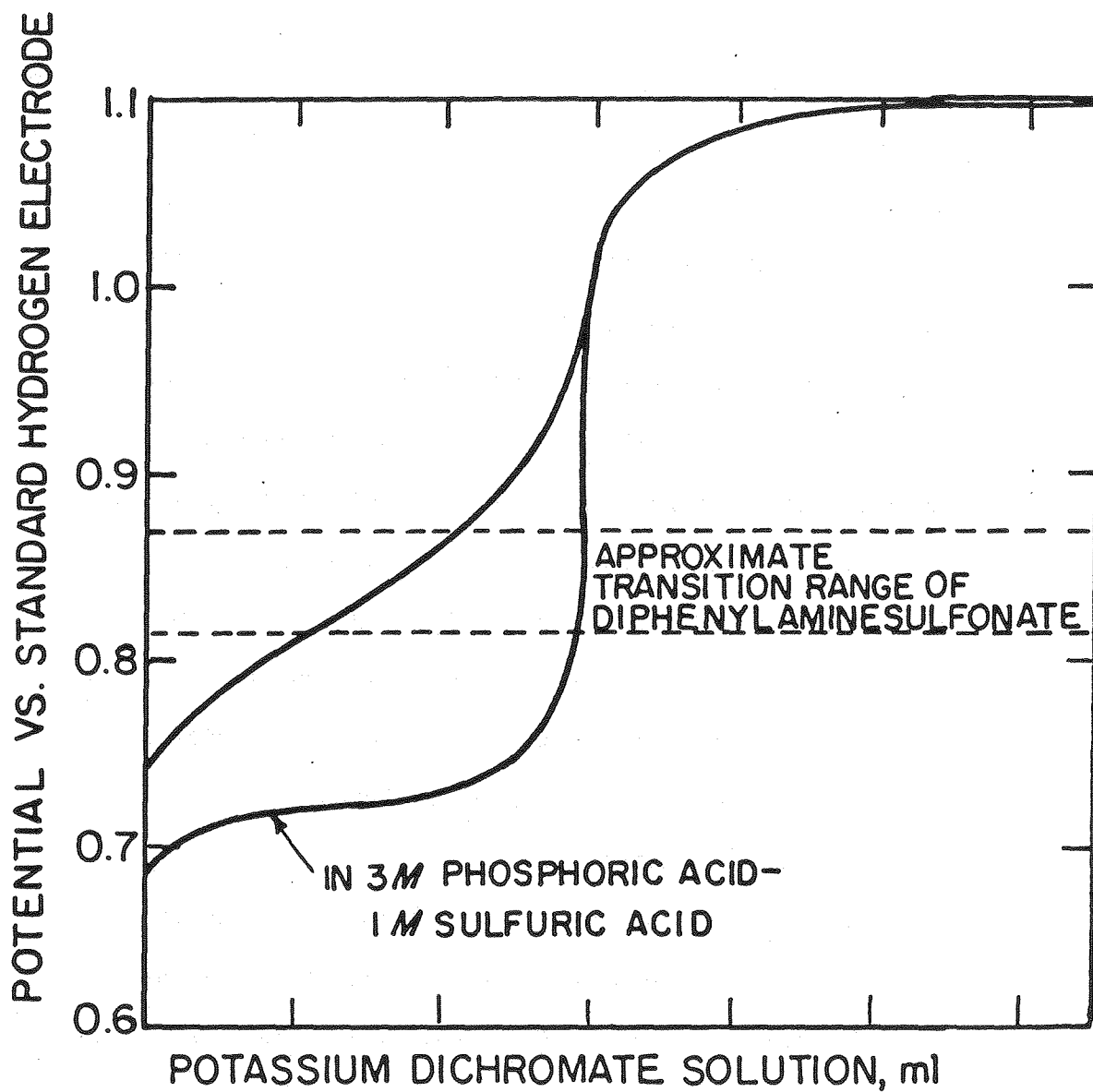


Figure 8. Effect of Phosphoric Acid - Sulfuric

Acid on the Titration of Iron (II) with Dichromate (after  
Fritz, ref. 19)

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#### 4. Gas Chromatography / Mass Spectroscopy

Gas Chromatograph analyses of products were made using a Finnigan 4000 Gas Chromatograph / E1-C1 Mass Spectrometer system with Nova 3 data system. A SP2250 capillary (open tubular) column was used. The temperature programmer was run at 50-250°C at a rate of 4°C/min. Helium was the carrier gas. Detection of peaks was done with a mass spectrometer, and spectra were compared to those in computer library files.

#### 5. Infrared Spectra

Infrared spectra of selected samples were obtained using a Perkin-Elmer 467 Grating Infrared Spectrophotometer. Mineral oil slurries were used for solid samples.

#### E. Experiments Performed

A complete listing of the reaction conditions for the oxidation experiments which were performed are given in tabular form. Experiments in which dibenzothiophene, diphenyl sulfide, and di-n-butyl sulfide were used as model compounds of coal sulfur groups are shown in Tables 11,12, and 13 respectively.

Table 11. Oxidation Experiments Using Dibenzothiophene (DBT).

Exp. No.	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Oxidants/ H <sub>2</sub> O 95% H <sub>2</sub> SO <sub>4</sub> · 7H <sub>2</sub> O Catalysts				DBT	Atmosphere	Agitation	Temp.	Run Duration
	H <sub>2</sub> O	95% H <sub>2</sub> SO <sub>4</sub>	· 7H <sub>2</sub> O	Catalysts					
DBT 1A	150 ml	4.51 ml	7.078 g	0.0 g	0.0 g	N <sub>2</sub>	300 RPM <sup>d</sup>	150°C	1 hr
" 1B	"	"	"	"	0.544	"	"	"	"
" 2A	"	6.44	20.244	"	0.0	"	"	"	"
" 2B	"	"	"	"	1.557	"	"	"	"
" 3A	"	8.47	35.959	"	0.0	"	"	"	"
" 3B	"	"	"	"	2.776	"	"	"	"
" 3E	"	"	"	"	"	"	590	"	4
" 3I	"	"	"	"	0.240	O <sub>2</sub> <sup>c</sup>	"	"	1
" 3J	"	"	"	"	"	"	"	"	4
" 4A	"	10.58	44.826	"	0.0	N <sub>2</sub>	300	"	1
" 4B	"	"	"	"	3.448	"	"	"	"
" 5A	"	12.79	51.008	"	0.0	"	"	"	"
" 5B	"	"	"	"	3.924	"	"	"	"
" 6A	"	15.11	56.955	"	0.0	"	"	"	"
" 6B	"	"	"	"	4.381	"	"	"	"
" 7A	"	18.16	56.507	"	0.0	"	"	"	"
" 7B	"	"	"	"	4.347	"	"	"	"
" 8A	"	28.54	35.263	"	0.0	"	"	"	"
" 8B	"	"	"	"	2.713	"	"	"	"
" 8C	"	"	"	"	"	"	"	"	4
" 8D	"	"	"	"	"	"	590	"	1
" 8F	"	0.0	0.0	"	0.240	O <sub>2</sub>	300	"	"
" 8G	"	28.54	35.263	"	"	"	"	"	"
" 8H	"	0.0	0.0	"	"	"	590	"	"
" 8I	"	28.54	35.263	"	"	"	"	"	"
" 8J	"	"	"	"	0.240	"	"	"	4
" 8M	"	"	"	a	"	"	"	"	1
" 8N	"	"	"	b	0.480	"	"	"	"
" 9A	"	41.22	21.251	0.0	0.0	N <sub>2</sub>	300	"	"
" 9B	"	"	"	"	1.635	"	"	"	"
" 10A	"	57.08	14.195	"	0.0	"	"	"	"
" 10B	"	"	"	"	1.092	"	"	"	"

Footnotes: a. 0.548 g MnSO<sub>4</sub> · H<sub>2</sub>O , 0.517 g CuSO<sub>4</sub> , 0.932 g ZnSO<sub>4</sub> · 7H<sub>2</sub>O

b. 0.758 g NH<sub>4</sub>VO<sub>3</sub>

c. 300 psia (20°C) of oxygen was charged into void space of bomb prior to all runs in which oxygen was used (430 psia at 150°C).

Table 12. Oxidation Experiments Using Diphenyl Sulfide (DPS).

Exp. No.	H <sub>2</sub> O	95% H <sub>2</sub> SO <sub>4</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	Catalysts/ Oxidants	DPS	Atm.	Agitation	T.	Run	
									Duration	
DPS 8D	150 ml	28.54 ml	35.263 g	0.0 g	1.174 g	N <sub>2</sub>	590 RPM	150°C	1 hr	
" 8H	"	0.0	0.0	"	0.932	O <sub>2</sub> a	"	"	"	
" 8I	"	28.54	35.263	"	"	"	"	"	"	
" 8J	"	"	"	"	"	"	"	"	4	
" 8K	"	"	"	0.548 MnSO <sub>4</sub> ·H <sub>2</sub> O 0.517 CuSO <sub>4</sub> 0.932 ZnSO <sub>4</sub> ·7H <sub>2</sub> O	"	"	"	"	1	

Footnote: a. Oxygen was loaded at 300 psia (20°C).

Table 13. Oxidation Experiments Using Di-n-Butyl Sulfide (DBS).

Exp. No.	H <sub>2</sub> O	95% H <sub>2</sub> SO <sub>4</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	Catalysts/ Oxidants	DBS	Atm.	Agitation	T.	Run	
									Duration	
DBS 8H	150 ml	0.0 ml	0.0 g	0.0 g	0.648 g	O <sub>2</sub> b	590 RPM	150°C	1 hr	
" 8L	"	28.54	35.263	a	3.893	N <sub>2</sub>	"	"	"	
" 8K	"	"	"	a	0.0	"	"	"	"	

Footnotes: a. 0.548 MnSO<sub>4</sub>·H<sub>2</sub>O , 0.517 CuSO<sub>4</sub> , 0.932 ZnSO<sub>4</sub>·7H<sub>2</sub>O

b. Oxygen was loaded at 300 psia (20°C).

A summary of the nomenclature (A - N) for the oxidation experiments is given in Table 14 for ease of reference.

Table 14. Summary of Nomenclature.

X = Present      O = Absent

Notation	Catalysts/ Oxidants	H <sub>2</sub> O	Acid	Iron	Organic Sulfide	Atmos.	(RPM) Agitation	(hr) Duration of Run
A	O	X	X	X	O	N <sub>2</sub>	300	1
B	O	X	X	X	X	N <sub>2</sub>	300	1
C	O	X	X	X	X	N <sub>2</sub>	300	4
D	O	X	X	X	X	N <sub>2</sub>	590	1
E	O	X	X	X	X	N <sub>2</sub>	590	4
F	O	X	O	O	X	O <sub>2</sub>	300	1
G	O	X	X	X	X	O <sub>2</sub>	300	1
H	O	X	O	O	X	O <sub>2</sub>	590	1
I	O	X	X	X	X	O <sub>2</sub>	590	1
J	O	X	X	X	X	O <sub>2</sub>	590	4
K	X <sup>a</sup>	X	X	X	O	N <sub>2</sub>	590	1
L	X <sup>a</sup>	X	X	X	X	N <sub>2</sub>	590	1
M	X <sup>a</sup>	X	X	X	X	O <sub>2</sub>	590	1
N	X <sup>b</sup>	X	X	X	X	O <sub>2</sub>	590	1

Footnotes: a. Mn<sup>+2</sup>, Cu<sup>+2</sup>, Zn<sup>+2</sup>.

b. VO<sub>3</sub><sup>-</sup>.



A listing of  $\text{ZnCl}_2$  experiments for desulfonation is given in Table 15.

Table 15. Desulfonation Experiments Using  $\text{ZnCl}_2$ .

<u>Exp. No.</u>	<u><math>\text{ZnCl}_2</math></u>	<u><math>\text{H}_2\text{O}</math></u>	<u><math>\text{FeCl}_3</math> <math>\cdot 6\text{H}_2\text{O}</math></u>	<u>Sulfone</u>	<u>Atm.</u>	<u>Agitation</u>	<u>T.</u>	<u>Run Duration</u>
ZN 1	302.833 g	10.0 g	8.0 g	1.280 g DBT $\cdot\text{O}_2$	$\text{N}_2$	300 RPM	200°C	1 hr
" 2	"	"	"	1.288 g DPS $\cdot\text{O}_2$	"	"	"	"
" 3	"	"	"	1.052 g DBS $\cdot\text{O}_2$	"	"	"	"

### III. RESULTS AND DISCUSSION

#### A. Experiments Using Dibenzothiophene

Dibenzothiophene (DBT) has a structure similar to the majority of organic sulfur groups in coal (condensed thiophenes). An extensive study was made of the conditions under which ferric iron in a sulfuric acid / water mixture might react with this model compound. Both nitrogen and oxygen atmospheres were used.

##### 1. Runs with a Nitrogen Atmosphere

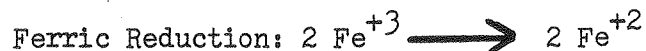
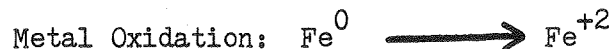
Initial investigations were performed with  $\text{Fe}^{+3}$  in solution under a nitrogen atmosphere. It was hoped that  $\text{Fe}^{+3}$  would be a strong and selective oxidant, so that conversion of dibenzothiophene to the sulfone or sulfoxide would occur.

Since any oxidation of organics would result in ferric iron ( $\text{Fe}^{+3}$ ) reduction, ferrous iron ( $\text{Fe}^{+2}$ ) concentration was measured at the end of each experiment. However, the aqueous mixture of water, ferric sulfate, and sulfuric acid is an extremely corrosive system. Even though a glass liner was used to protect the interior wall of the bomb, it was necessary to determine whether corrosion of internal parts was possible. This corrosion would lead to formation of  $\text{Fe}^{+2}$ , affecting results.

For this reason, "base" runs for each acid condition were performed first, prior to actually attempting to oxidize dibenzothiophene. In these initial experiments, runs 1A - 10A, no model compound was added. Total iron and  $\text{Fe}^{+2}$  in solution were measured at the end of a "base" run. If total iron was constant compared to the initial iron, but  $\text{Fe}^{+2}$  was found, oxidation of non-iron reactor internals by corrosion could have been the cause.

This oxidation would have reduced ferric iron to ferrous iron.

On the other hand, if the total iron in solution increased by one-third the amount of  $\text{Fe}^{+2}$  measured, oxidation of  $\text{Fe}^0$  in the stainless steel internals could have been the cause:



If the total iron increased by an amount less than one-third the  $\text{Fe}^{+2}$  observed, both corrosion of iron and non-iron internals could have occurred. Ferric sulfate which precipitated from the solution was also measured after a run to complete the iron material balance.

This series of "base" runs was then used as a correction in the model-compound runs. Ferrous iron produced by oxidation of internals was subtracted from the  $\text{Fe}^{+2}$  measured after an experiment with organics. In this way the actual conversion of  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  due to organic oxidation could be determined.

The range of acid concentrations both for base runs, 1A - 10A, and for model-compound runs, 1B - 10B, is shown in Figure 9. The experiments were performed over a wide range of acid concentrations, with the purpose of defining the most effective acid condition. The percent saturation for the ten acid conditions ranges from 35.9 to 50.6%. All of the model-compound oxidation experiments were run at one of the ten concentrations shown in Figure 9. The  $\text{SO}_4^{-2}/\text{Fe}^{+3}$  mole ratios for these ten acid concentrations are given below. The  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{SO}_4$  wt-% relative to  $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$  can be read directly from Figure 9 for the ten run conditions.

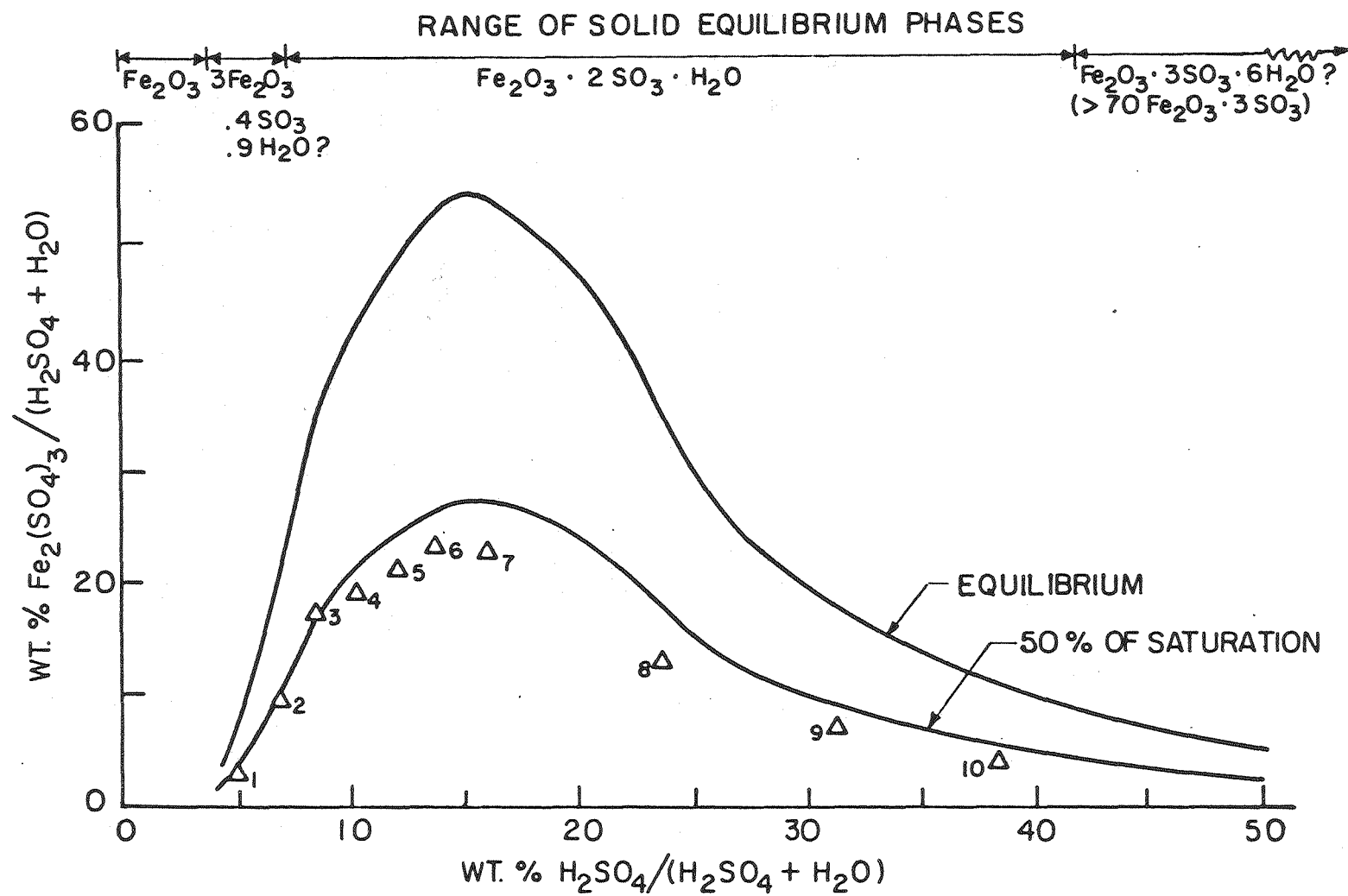


Figure 9. Range of Acid Concentrations for the Experiments.

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Table 16. Sulfate to Ferric Iron Ratios (mole) for the Various Acid Concentrations.

Acid Condition (Fig. 9)	Experiments Performed	$\text{SO}_4^{-2}/\text{Fe}^{+3}$ Initial Mole Ratio
1	1A , 1B	4.47
2	2A , 2B	2.99
3	3A , 3B	2.60
4	4A , 4B	2.61
5	5A , 5B	2.68
6	6A , 6B	2.74
7	7A , 7B	3.01
8	8A , 8B	5.29
9	9A , 9B	10.60
10	10A , 10B	20.31

The hydration of ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ) was calculated by measuring the total dissolved iron in each solution and comparing this to the actual ferric sulfate added to the water and sulfuric acid mixtures. Table 17 shows that x ranged from 5.9 to 14.2. An average value was calculated, discarding high and low values, for use in future runs. This average for x, the moles of water per mole of  $\text{Fe}_2(\text{SO}_4)_3$ , is 7.0.

Table 17. Calculation of Ferric Sulfate Hydration (x).

Experiment Performed	Dissolved $\text{Fe}_2(\text{SO}_4)_3 \cdot$ $x\text{H}_2\text{O}$	Total Fe Measured in Solution	$\text{Fe}_2(\text{SO}_4)_3$ Calculated	$\text{H}_2\text{O}$ Calculated	x Calculated
1A	7.078 g	1.446 g	5.168 g	1.910 g	8.19
2A	20.244	4.188	14.966	5.278	7.81
3A	35.959	7.924	28.320	7.639	5.98
4A	44.826	9.859	35.333	9.593	6.03
5A	51.008	11.268	40.270	10.739	5.91

Table 17 (cont.)

Exp. Per- formed	Dissolved $\text{Fe}_2(\text{SO}_4)_3 \cdot$ $x\text{H}_2\text{O}$	Total Fe Measured in Solution	$\text{Fe}_2(\text{SO}_4)_3$ Calculated	$\text{H}_2\text{O}$ Calculated	x Calcu- lated
6A	56.955 g	9.702 g	34.673 g	22.281 g	14.24
7A	56.507	10.975	39.222	17.286	9.76
8A	35.263	7.581	27.044	8.169	6.68
9A	21.251	4.743	16.949	4.301	5.62
10A	14.195	3.333	11.912	2.282	4.25

From the oven drying of  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  samples, x was determined as follows:

Oven Temp.	Time	x Calculated
120°C	21 hr	2.63
160	4	3.74
175	5	4.37

Obviously not all the water was removed in drying, but higher temperatures yielded an x which approached  $x = 7.0$ . Ferric sulfate is normally found as  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  ( $x = 9$ ) or  $\text{Fe}_2(\text{SO}_4)_3$  ( $x = 0$ )<sup>14</sup>. The value of  $x = 7.0$  may reflect a mixture of the two. This value is therefore used in subsequent calculations, since iron in solution was not measured prior to all runs.

a. Results of Base Runs in Nitrogen at Moderate Conditions

The results of the base runs are given in Table 18. These experiments were all performed at moderate stirring speeds (300 RPM) and reaction time (1 hr) under a nitrogen atmosphere at 150°C. Sulfuric acid, water, and ferric sulfate were the only reactants.

Table 18. Iron Analysis Results from Base Runs 1A - 10A.

Exp. No.	Fe <sup>+3</sup> Initial in Solution	Fe Total Final in Solution	Fe <sup>+2</sup> Final Fe <sup>+3</sup> Initial x 100	Fe as Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 7H <sub>2</sub> O prec.	Fe Fin. Fe Init. x 100
1A	1.486 g	1.392 g	0.714 %	0.0 g	93.6 %
2A	4.251	3.915	0.934	0.0	92.1
3A	7.555	7.398	0.453	0.166	100.1
4A	9.420	8.585	0.853	0.481	96.2
5A	10.722	9.359	0.983	0.753	94.3
6A	11.975	9.070	0.614	0.339	78.6
7A	11.883	10.098	0.481	0.172	86.4
8A	7.426	7.656	1.292	0.0	103.2
9A	4.471	5.012	9.466	0.0	112.1
10A	2.998	3.254	3.089	0.0	108.9

An overall mass balance on iron from these runs was calculated from total iron in solution after a run (column 3) plus iron as precipitate (column 5) compared to iron as Fe<sup>+3</sup> initially (column 2). We see in column 6 that closing this mass balance was reasonably good for most runs. Only the high-acid runs, 9A and 10A, showed any significant increase in total iron.

Apparently oxidation of non-iron (most likely Ni and Cu) occurred in runs 1A and 8A, with some iron oxidation also occurring in runs 9A and 10A. We would expect the Fe<sup>+2</sup> in runs 9A and 10A to be three times the total iron increase if Fe<sup>0</sup> oxidation was the only problem. With oxidation of non-iron internals too, Fe<sup>+2</sup> would exceed the total iron increase by more than three times. Runs 9A and 10A show Fe<sup>+2</sup> less than the total iron increase.

Since overall mass balance accuracy is 0.1 to 21.4% for the low-acid runs, total iron for the high-acid runs could be in error

by a significant amount. The  $\text{Fe}^{+2}$  measurements were less than the total iron increases, so that we cannot provide any quantitative comparison of iron versus non-iron oxidation. In any event, we can say that oxidation of internals does occur at both high and low acid concentrations. Severe corrosion and oxidation of  $\text{Fe}^0$  is significant only at high acid conditions. This is confirmed by visual inspection of internals which were severely corroded at the highest acid conditions (10A).

Since it is difficult to close the mass balance quantitatively, base measurements of  $\text{Fe}^{+2}$  due to  $\text{Fe}^{+3}$  reduction or internals oxidation were simply subtracted from those for organic oxidation runs. When an organic experiment was run for a period of time longer than the 1-hour base run, the  $\text{Fe}^{+2}$  subtracted was increased by the ratio of the run lengths. In this way we could more accurately determine whether an actual run exhibited  $\text{Fe}^{+3}$  reduction above what we would expect due to corrosion.

b. Results of Organic Runs in Nitrogen at Moderate Conditions

Results from the organic oxidation runs under a  $\text{N}_2$  atmosphere are given in Table 19. All ten of these runs were performed at moderate conditions of 300 RPM, 1 hour, and  $150^\circ\text{C}$ , as for the base runs.



Table 19. Iron Analysis from Runs 1B - 10B.

Exp. No.	Fe Total Final in Solution	$\frac{\text{Fe}^{+2}\text{Final}}{\text{Fe}^{+3}\text{Initial}} \times 100$	Fe as Precipitate (from base runs)	$\frac{\text{Fe Total Final}}{\text{Fe Total Init.}} \times 100$
1B	1.401 g	0.875 %	0.0	94.3 %
2B	3.768	0.887	0.0	88.6
3B	4.655	0.753	0.166	63.8
4B	8.729	0.658	0.481	97.8
5B	7.778	0.755	0.753	79.6
6B	9.869	0.631	0.339	85.2
7B	10.189	0.679	0.172	87.2
8B	7.855	0.855	0.0	105.9
9B	4.839	2.975	0.0	108.3
10B	3.980	38.888	0.0	133.2

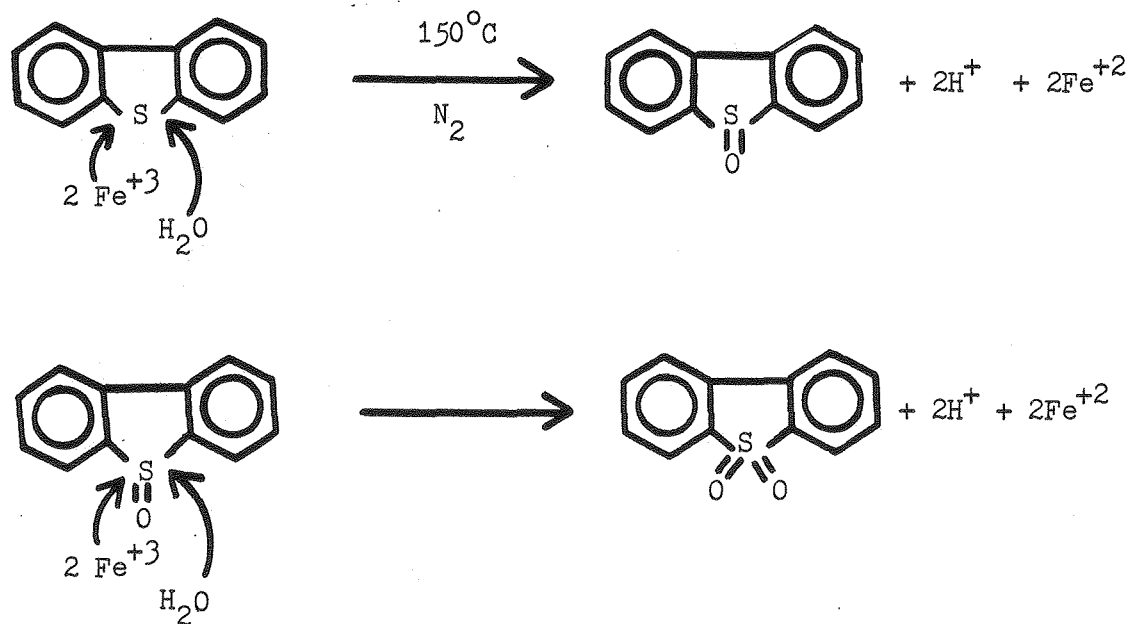
Again we see significant total iron increases at high acid concentration, but no total iron increases for low acid runs. Run 10B, with a 32.2% increase in total iron, showed severe shaft and impeller corrosion. Only run 10B had a  $\text{Fe}^{+2}$  measurement in excess of the total increase in iron. This amount of  $\text{Fe}^{+2}$  was less than three times the increase in total iron, so that we cannot quantitatively compare iron to non-iron corrosion. Note, however, that this run showed a maximum reduction (column 3) of 38.9% of the initial  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$ . Since the total iron increase for this run was 33.2%, corrosion of iron was probably significant and little organic oxidation actually occurred.

We see that, except for the high acid runs with severe corrosion, both base and actual runs show roughly 1% reduction of  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  during a run. The corrected  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  conversion (subtracting base run values) are given in Table 20.

Table 20. Corrected  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  Conversion for Organic Oxidation Runs.

Experiment Number	$\frac{\text{Fe}^{+2} \text{ Final}}{\text{Fe}^{+3} \text{ Initial}} \times 100 = \text{Corrected Iron Conversion}$
1B	0.161 %
2B	-0.047
3B	0.300
4B	-0.195
5B	-0.228
6B	0.017
7B	0.198
8B	-0.437
9B	-6.495
10B	35.801

The maximum positive conversion in the runs (neglecting run 10B where severe corrosion occurred) is 0.3%. For the following oxidation reactions:



we calculate an overall  $\Delta G_{\text{sulfide to sulfone}} = -90 \text{ kcal/mole}$

If we had oxidation of dibenzothiophene to sulfoxide or on to sulfone, we would produce two moles of  $\text{Fe}^{+2}$  for each mole of oxygen atoms added to the dibenzothiophene molecule. Since the  $\text{Fe}^{+3}$ : Dibenzothiophene mole ratio was 9.1 to 1 for all ten experiments, we would need 22% conversion of ferric to ferrous iron to convert all of the dibenzothiophene to sulfoxide. For complete conversion to sulfone we would need 44% conversion.

Since our highest conversion (neglecting run 10B) of ferric to ferrous iron was  $0.30\% \pm .01\%$ , the most optimistic conversion to sulfone is 0.68%. The iron analysis thus shows that there was essentially no oxidation of dibenzothiophene in a nitrogen atmosphere.

The organic products of the ten runs were analyzed to determine whether oxidation occurred. Oxygen weight percent possible in the sample was calculated by difference based on carbon, hydrogen, and sulfur weight percent analyses.

The results of these tests showed a maximum possible oxygen weight percent ranging from 0.035 to 0.26 wt-%. Only five samples, runs 1B, 2B, 6B, 9B, and 10B, could have contained any oxygen. Of these, the organic residue from run 1B could have contained the most oxygen, 0.26 wt-%. Since the error was 0.3 wt-% for each C, H, or S measurement, this value is insignificant. Even if the measurements were precise, 0.26 wt-% oxygen would represent only a 1.5% oxidation of the dibenzothiophene in the sample to sulfone.

The results of analyses for iron and organic residue from runs 1B to 10B showed that no appreciable reaction occurred at any acid condition. Residual iron in the organic material recovered

was quite low. Most of the original organic was retrieved after a run, with minor losses due to filtering and handling. There were no ether-extractable organics in the aqueous phase of any of the runs.

c. Results of Organic Runs in Nitrogen at More Severe Conditions

Since our experiments under moderate conditions of 1 hour at 300 RPM had no effect on dibenzothiophene, more severe conditions were tried. This reaction is thermodynamically feasible, so longer runs were made in an attempt to obtain a measureable rate. Higher agitation was used to improve organic / aqueous contact in case mass transfer rates were limiting. Higher temperatures (above 150°C) were not attempted since we desired relatively mild reaction conditions (to avoid coal oxidation in any industrial application).

As no particular acid concentration seemed optimal, concentrations 3 and 8 on Figure 9 were selected as low-acid and high-acid conditions for these runs. A  $\text{Fe}^{+3}$ /Dibenzothiophene ratio (mole) of 9.1 was used throughout. Results of these runs are given in Table 21.

Table 21. Results of Experiments at More Severe Conditions.

Exp. No.	$\text{Fe}^{+2}_{\text{Final}}$ $\text{Fe}^{+3}_{\text{Init.}}$ x 100	$\text{Fe Total Fin.}$ $\text{Fe Total Init.}$ x 100	$\text{Fe}^{+2}_{\text{Fin.}}$ $\text{Fe}^{+3}_{\text{Init.}}$ (corrected) x 100	RPM	Duration	Oxygen wt-% Possible in Organic Residue
3E	6.39 %	100.5 %	4.58 %	590	4 hr	0.0 wt-%
8C	6.66	92.3	1.49	300	4	0.0
8D	2.68	107.5	1.39	590	1	0.12

For the low-acid condition, run 3E, we see a corrected  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  conversion (column 4) of 4.58%. We could have a maximum conversion of 10.4% of the dibenzothiophene to sulfone based on this analysis. Total iron did not increase significantly. Since this was a four-hour run at high RPM, internal oxidation could have been quite high. The analysis of the organic residue showed no oxygen present.

The results for the high-acid runs show only 1.39% corrected iron conversion for the 1 hr run at high RPM (run 8D). This corresponds to 3.16% oxidation of dibenzothiophene to sulfone. Oxygen analysis by difference for this run showed 0.12 wt-% oxygen as a maximum, which corresponds to 0.75% conversion to sulfone.

The results for the high-acid run for 4 hours at moderate RPM show only 1.49% corrected conversion of  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$ , or 3.39% oxidation to sulfone as a maximum. Organic analysis showed that no reaction occurred.

We can therefore conclude that oxidation of dibenzothiophene by  $\text{Fe}^{+3}$  in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  under  $\text{N}_2$  at mild conditions ( $150^\circ\text{C}$ ) was severely limited, either kinetically or by mass-transfer. Decreasing mass-transfer limitations and increasing residence time substantially had no effect on this unreactive system at either high or low acid conditions.

## 2. Runs with an Oxygen Atmosphere

Oxygen pressure was used in an attempt to observe oxidation. Ferric iron was also used in these experiments. All runs were performed at  $150^\circ\text{C}$  with an initial charge of 300 psia  $\text{O}_2$

(433 psia  $O_2$  pressure at run temperature). Oxygen was in very large excess to that required for complete oxidation of the dibenzothiophene to sulfone in all runs.

Prior to performing the  $Fe^{+3}/H_2SO_4$  runs, experiments with oxygen and dibenzothiophene in water were performed. The results of these experiments are given in Table 22. A C, H, and S analysis of the products of these runs were used to determine oxidation possible.

Table 22. Results of Dibenzothiophene, Water and Oxygen Experiments.

Experiment Number	RPM	Duration	Oxygen Wt-% Possible in Organic Residue
8F	300	1 hr	0.53 wt-%
8H	590	1	0.42

With 0.53 wt-% maximum oxygen possible in the organic residue (run 8F), we could at most have 3.09% conversion to sulfone. It appears that dibenzothiophene is quite refractory to oxidation at 433 psia oxygen pressure. Increased rate of stirring had no effect.

In order to investigate any catalytic effect of  $Fe^{+3}$ , or increased oxygen-transfer characteristics due to iron, several runs with  $Fe^{+3}$  and  $O_2$  were performed. The results of these experiments at high-acid and low-acid concentrations are given in Table 23.

Table 23. Results of Dibenzothiophene Experiments with  $\text{Fe}^{+3}$  and  $\text{O}_2$ .

Exp. No.	RPM	Duration	Oxygen Wt-% Possible in the Organic Residue	$\text{Fe}^{+3}$ /DBT mole ratio	$\text{Fe}^{+2}$ Final $\text{Fe}^{+3}$ Final in Solution	Fe Total Final Fe Total Initial x 100
3I	590	1 hr	1.65 wt-%	105.3	0.0015	112.6 %
3J	300	4	0.6	105.3	0.004	112.6
8G	300	1	0.0	103.3	0.005	-
8I	590	1	0.0	103.3	0.004	108.5
8J	590	4	1.09	103.3	0.005	105.4

Conversion of  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  was not calculated for any run, since the oxygen atmosphere would oxidize  $\text{Fe}^{+2}$  back to  $\text{Fe}^{+3}$ . Final ferrous to ferric ratios were quite low for this reason. All runs showed a total iron increase, revealing substantial corrosion. Any ferrous present was most likely a result of the corrosion of internals. The highest oxygen possible in the residue was 1.65 wt-% (Run 3I). This corresponds to 10.1% oxidation to sulfone. However, from the carbon and hydrogen analyses we see a C/H ratio of 16.985 for this run. Unreacted dibenzothiophene or the sulfone have a C/H ratio of 17.874. The 1.65 wt-% oxygen by difference may be due to impurities in the residue. The four-hour low-acid run (3J) had only a 0.6 wt-% oxygen possible (3.59% conversion to sulfone) with a C/H ratio of 17.486. It would therefore appear that little or no oxidation occurred in either run.

The high-acid runs showed no oxidation possible until 4 hours

at high RPM (Run 8J). With an oxygen content of 1.09 wt-%, the conversion possible to sulfone is 6.51% at a C/H ratio of 16.188. This looks like impurities (such as iron oxides or metal sulfates), with no actual conversion to sulfone.

It thus appears that the oxygen-ferric iron system is kinetically limited. High stirring speed and long residence times are not sufficient to show oxidation of dibenzothiophene. In an attempt to improve the kinetics, potentially catalytic metals were added to the oxygen and iron system. Manganese ( $Mn^{+2}$ ), copper ( $Cu^{+2}$ ), and zinc ( $Zn^{+2}$ ) were added as 5 mole % of the initial ferric iron concentration in run 8M. Vanadium (as  $VO_3^-$ ) was also added in experiment 8N as a strong inorganic oxidant. Results are given in Table 24.

Table 24. Experiments with Catalytic or Oxidative Additives.

Exp. No.	RPM	Dur- ation	Oxygen wt-% Possible in Org. Residue	$Fe^{+3}/DBT$ mole ratio	$\frac{Fe^{+2}}{Fe^{+3}}$ Final in Soln.	$\frac{Fe\ Total\ Final}{Fe\ Total\ Init.}$ x 100
8M	590	1 hr	0.64 wt-%	103.3	0.004	103.7 %
8N	590	1	6.36	51.6	0.0	106.9

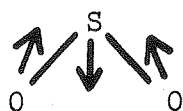
The 0.64 wt-% oxygen for the catalytic additive run (8M) yields 3.76% as a maximum conversion to sulfone. Obviously, catalysts such as  $Zn^{+2}$ ,  $Mn^{+2}$ , and  $Cu^{+2}$  offer no increase in dibenzothiophene oxidation rate for the iron/oxygen system.

For the one run with ammonium metavanadate (8N), we see a 6.36 wt-% possible oxygen content in the residue. We calculate 39.9% conversion to sulfone based on microanalysis. The C/H

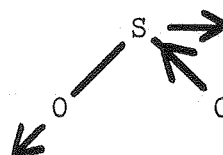


ratio for this residue is 17.316, very close to the 17.874 ratio for either sulfone or unreacted dibenzothiophene. It would appear that we have a mixture of dibenzothiophene and some oxidized dibenzothiophene. The melting point of the residue is  $139 - 154^{\circ}\text{C}$ . The m.p. range for dibenzothiophene is  $99 - 100^{\circ}\text{C}$ ; for sulfone the m.p. range is  $231 - 233^{\circ}\text{C}$ . We would expect a eutectic (melting point depression) for a mixture of dibenzothiophene and the sulfone, so this temperature range, well above  $100^{\circ}\text{C}$ , suggests that we do indeed have a large amount of sulfone. There was no vanadium present in the residue.

Infrared analysis is generally a useful tool in determining the presence of sulfur-oxygen bonds. There is a good deal of literature published on the distinctive infrared group frequencies of the sulfones.<sup>16,38</sup> The two major absorption bands are from  $1120-1160\text{ cm}^{-1}$  and  $1300-1350\text{ cm}^{-1}$ . These bands are caused by symmetric and non-symmetric stretch of the  $\text{SO}_2$  group as below<sup>9</sup>:



Symmetric stretch  
 $1120-1160\text{ cm}^{-1}$



Non-symmetric stretch  
 $1300-1350\text{ cm}^{-1}$

These absorption characteristics are shown for a variety of sulfones in Table 25.

Table 25. Vibrational Frequencies of the  $\text{-SO}_2\text{-}$  Group in Various Sulfones (After Robinson, ref. 36).

Sulfones $\text{RR'SO}_2$	$\text{SO}_2(\text{sym})$	$\text{SO}_2(\text{asym})$
Methyl ethyl sulfone	1145 $\text{cm}^{-1}$	1330 $\text{cm}^{-1}$
Dibutyl sulfone	1139	1330
Methyl propyl sulfone	1139	1299-1316
Diphenyl sulfone	1158	1319
Phenyl benzyl sulfone	1155	1325
Phenyl methyl sulfone	1160	1334
Dibenzyl sulfone	1155	1325
Phenyl vinyl sulfone	1153	1324
Methyl vinyl sulfone	1139	1312
Methyl allyl sulfone	1136	1307
Phenyl allyl sulfone	1150	1325
Cyclohexyl methyl sulfone	1144	1321
Dicyclohexyl sulfone	1130	1312

In general, more modern analytical techniques such as nuclear magnetic resonance, thin layer chromatography, or analysis of mass spectra are better methods for detecting sulfoxide and sulfone. Since our major aim was to investigate a number of compounds under a wide range of conditions, we were interested in defining the maximum conversion possible, rather than systematically identifying small quantities of various products.

Infrared analysis was performed on pure samples of dibenzothiophene and dibenzothiophene sulfone, as well as the organic residue from run 8N. The spectra are given in Figure 10. Neither the sulfone or run 8N have any significant peaks relative to the sulfide in either the  $1120\text{-}1160\text{ cm}^{-1}$  or  $1300\text{-}1350\text{ cm}^{-1}$  regions. Although we don't see the characteristic bands for the sulfonyl group, we do see a peak in the  $750\text{ cm}^{-1}$  region for both run 8N and the sulfone. The spectra from run 8N show an intermediate intensity in this region, compared to the parent compound and the sulfone.

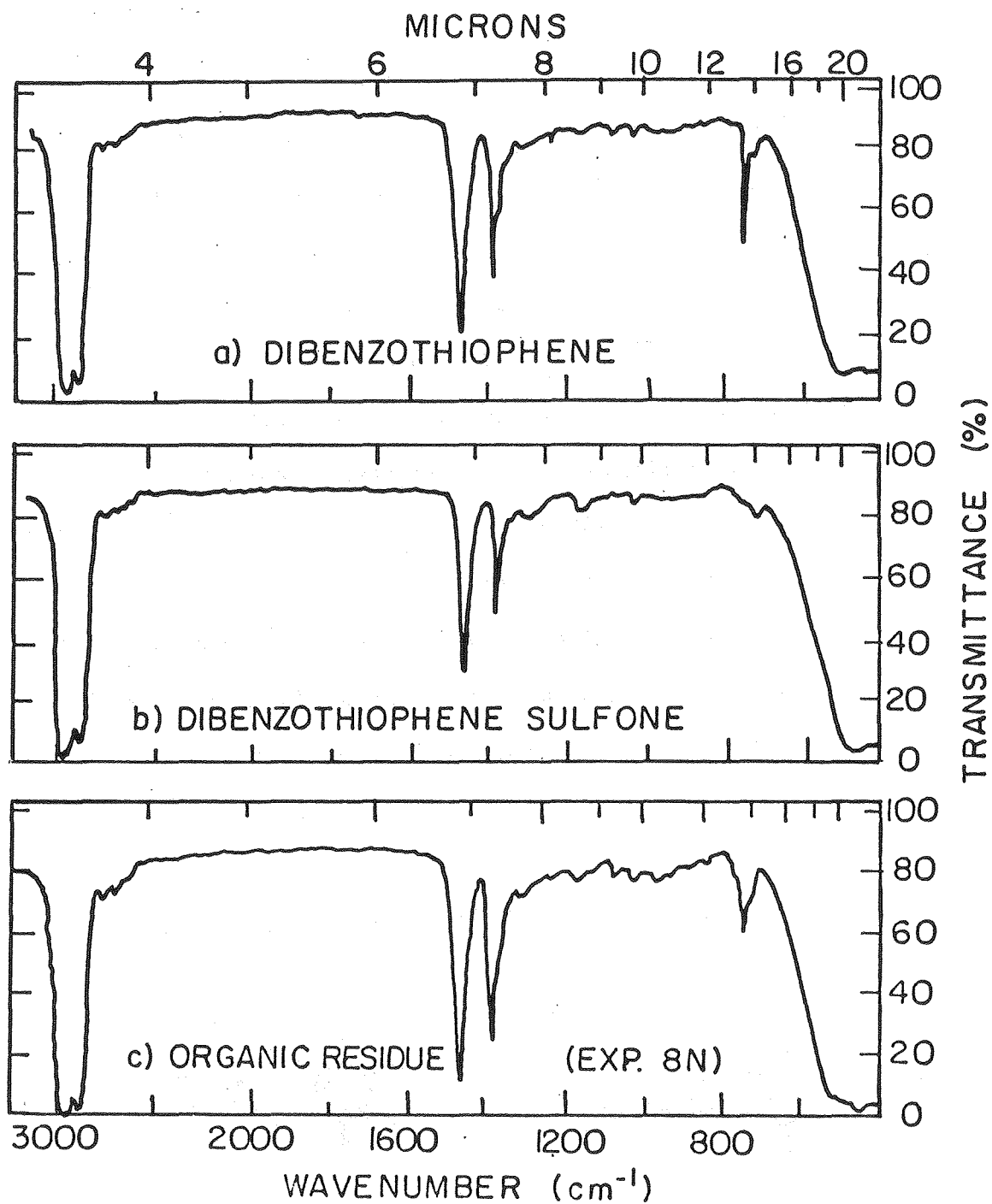


Figure 10. Infrared Spectra.

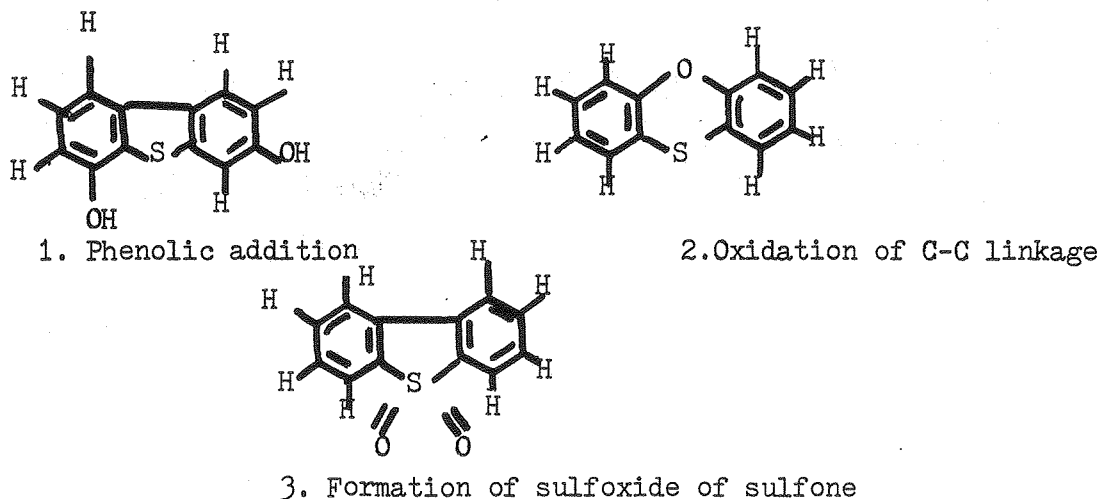
XBL 807-5418

The rest of the spectra for these samples have similar intensities in the same regions. Based on the  $750\text{ cm}^{-1}$  intensities, it would appear that we have 33% sulfone in sample 8N. This correlates very well with the 40% estimate based on micro-analysis for this run.

Since run 8N also had the correct C/H ratio for direct oxidation of sulfur, our conclusions for vanadium oxidation are more optimistic. We can conclude that some oxidation occurred, possibly as phenolic additions to the matrix, oxidation of carbon-carbon linkages, or as selective oxidation of sulfur. Figure 11 shows these possible types of products.

A listing of the organic analysis of the residue from run 8N is given in Appendix A, along with the C, H, and S analyses for pure dibenzothiophene and sulfone for comparison.

Figure 11. Suggested Products, Run 8N with Metavanadate Added.



## B. Experiments with Diphenyl Sulfide (DPS)

Since dibenzothiophene appeared to be quite refractory to oxidation (except with a large oxidation potential, using metavanadate), additional experiments with simpler sulfides were warranted. Diphenyl sulfide is an aryl sulfide, representative of the sulfide bridges which connect aromatic coal groups.

### 1. Experiments with $\text{Fe}^{+3}$ under Nitrogen or Oxygen

Results for runs with iron are given in Table 26. One run was under a nitrogen atmosphere at  $150^{\circ}\text{C}$  (8D), the remainder were under 433 psia oxygen at  $150^{\circ}\text{C}$ . All of the experiments were performed at high RPM (590) at high-acid concentration, while reaction time was varied. A very large excess of oxygen relative to diphenyl sulfide was used in experiments 8I and 8J.

Table 26. Diphenyl Sulfide Runs in  $\text{Fe}^{+3}$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4$ .

Exp. No.	Duration	Wt-% in Organic Residue	Oxygen (mole)		$\frac{\text{Fe}^{+2}}{\text{Fe}^{+3}}$ Final	$\frac{\text{Fe}^{+2}}{\text{Fe}^{+3}}$ Initial	Atmosphere
			$\text{Fe}^{+3}$	DPS			
8D	1 hr	- wt-%	20.9	0.0295	105.3 %		Nitrogen
8I	1	2.19	26.1	0.0065	105.9		Oxygen
8J	4	8.76	26.1	0.0083	98.5		Oxygen

The corrected (subtracting base run 8A)  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  conversion for run 8D is 1.72%. This corresponds to a possible diphenyl sulfide to sulfone conversion of 9.17%. Based on iron analysis, it appears we have some reaction under  $\text{N}_2$ . Since an organic analysis was not performed, this cannot be confirmed by oxygen analysis. Run 8I, using oxygen, showed 2.19 wt-% oxygen possible in the residue,

or 12.5% conversion to diphenyl sulfone. Run 8J, also in an oxygen atmosphere, showed 8.76 wt-% oxygen in the residue after 4 hours. This corresponds to 59.1% oxidation to sulfone, roughly four times that for the one-hour run. The maximum oxygen possible in run 8H, using only  $O_2$  and diphenyl sulfide without iron for 1 hour, was 0.41% oxygen. This corresponds to 2.4% sulfone formation. Apparently both the  $Fe^{+3}/N_2$  and  $Fe^{+3}/O_2$  runs at 1 hour were capable of much more oxidation.

The C/H ratio for run 8I is 13.797; for run 8J it is 13.018. For direct sulfur oxidation to sulfone we would expect C/H ratios of 14.299. Since the C/H ratios are low for the products, and since ether was used as a solvent, some oxygen from solvent impurities may have been present.

For this reason, GC/MS was performed on the organic material from run 8J. This analysis showed a good library fit for two peaks as diphenyl sulfide and phenyl sulfoxide. Phenyl sulfone was selected as a strong possibility for the third peak. A fourth peak was identified as either dibenzothiophene or dibenzothiophene sulfoxide. Ether was also identified.

The C/H ratio for dibenzothiophene and dibenzothiophene sulfoxide is 17.874, while that for diphenyl sulfide, sulfoxide, or sulfone is 14.299. The value of 13.018 found in this analysis is a bit low. Ether has a C/H ratio of only 5.296. Small amounts of this organic would lower our overall C/H ratio.

It thus appears that diphenyl sulfide can be oxidized at  $150^{\circ}C$  in the presence of 433 psia oxygen, .42 M  $Fe_2(SO_4)_3$  and 3.2 M  $H_2SO_4$

(23.7 wt-%  $\text{H}_2\text{SO}_4/(\text{H}_2\text{SO}_4 + \text{H}_2\text{O})$  and 12.7 wt-%  $\text{Fe}_2(\text{SO}_4)_3/(\text{H}_2\text{SO}_4 + \text{H}_2\text{O})$ ). The oxidation appears to be selective since diphenyl sulfoxide was identified as a product. Diphenyl sulfone and dibenzothiophene sulfoxide were also possibilities for products which would show selectivity. The organic analysis, as well as an analysis of the GC/MS spectra for these runs is given in Appendix B.

## 2. Experiments with $\text{Fe}^{+3}$ and Catalysts

In order to reduce the residence time required for oxidation,  $\text{Mn}^{+2}$ ,  $\text{Zn}^{+2}$ , and  $\text{Cu}^{+2}$  as 5 mole % of the  $\text{Fe}^{+3}$  were added as catalysts. The results of this run are given in Table 27. This run was at  $150^\circ\text{C}$  with 433 psia  $\text{O}_2$ .

Table 27. Results of Addition of Catalysts.

Exp. No.	Duration	Oxygen Wt-% Possible in Organic Residue	$\text{Fe}^{+3}$ DPS	$\text{Fe}^{+2}$ Final $\text{Fe}^{+3}$	$\frac{\text{Fe Total Fin.}}{\text{Fe Total Init.}} \times 100$
8M	1 hr	1.28 wt-%	26.1	0.0047	91.5 %

The estimated addition of 1.28 wt-% oxygen corresponds to 7.63% conversion to diphenyl sulfone; there appeared to be no improvement over the oxidation without "catalysts". The C/H ratio for this sample was 14.170, very close to the value of 14.299 expected for either diphenyl sulfide or sulfone. A GC/MS analysis was not helpful for this sample. Only one peak, identified as diphenyl sulfide, was observed. Obviously zinc ( $\text{Zn}^{+2}$ ), manganese ( $\text{Mn}^{+2}$ ), and copper ( $\text{Cu}^{+2}$ ) had no catalytic effect.

### C. Experiments with Di-n-Butyl Sulfide (DBS)

Since the iron-oxygen system at 150°C appears to oxidize a good deal of the diphenyl sulfide to sulfone after 4 hours, we would hope that other "simple" sulfides could be selectively oxidized. For this reason, di-n-butyl sulfide was used as a model for aliphatic or alicyclic sulfides in coal.

Several experiments were performed at 150°C and 590 RPM, with ferric iron and 5 mole-% of Zn, Mn, and Cu (as divalent ions) added together as catalysts under nitrogen. Since DBS has a high vapor pressure at 150°C, runs with O<sub>2</sub> were unsuccessful because of rapid combustion in the gas phase. The Fe<sup>+3</sup>/DBS ratios were varied. Results are given in Table 28.

Table 28. Results of Di-n-Butyl Sulfide Runs in a Fe<sup>+3</sup>/Catalyst System Under N<sub>2</sub>.

Exp. No.	Duration	DBS Fe <sup>+3</sup>	Fe <sup>+2</sup> Final Fe <sup>+3</sup> Initial	x 100	Fe Total Final Fe Total Initial	x 100
8L(A)	1 hr	0.02	6.08	%	97.1	%
8L(B)	1	0.066	17.07		88.8	
8L(C)	1	0.2	27.47		94.3	

There appears to be a direct relationship between conversion of Fe<sup>+3</sup> to Fe<sup>+2</sup> (column 4) and increasing DBS concentration (column 3). This trend would indicate that a reaction is occurring with conversion of Fe<sup>+3</sup> to Fe<sup>+2</sup> dependent on DBS available. Since the total iron did not increase for any run, the large conversion of Fe<sup>+3</sup> to Fe<sup>+2</sup> points to significant reaction. A base run, 8K, was



run with iron, catalysts, and oxygen with no di-nibutyl sulfide. This run showed 6.2% total iron increase, with  $\text{Fe}^{+2}/\text{Fe}^{+3}$  conversion of 1.63%. All three runs with DBS had significantly greater conversion values than this base run. The corrected conversions (subtracting base conversion) are 4.45, 15.44, and 25.84 % for the three runs at DBS/ $\text{Fe}^{+3}$  ratios of 0.02, 0.066, and 0.2 respectively. Of we have sulfone formation, the three runs would yield 112.4%, 116.6%, and 64.6% conversion to sulfone. Within our analytical error, it appears we could have almost complete oxidation of DBS to sulfone in one hour. There appears to be little relationship between DBS concentration and the rate of the reaction (whether sulfone formation or not).

The GC/MS was used to identify the products of the  $\text{Fe}^{+3}$ /catalyst reaction. The results (see Appendix C) of that analysis for run 8L(C) showed no sulfones. Ether (impurity from separation technique), 1-butanethiol, di-n-butyl sulfide, and butene were identified. Apparently the reaction which occurred was not sulfonation, but merely cracking of one of the sulfur-carbon bonds to form butene and butanethiol. It would appear that ferric iron (possibly aided by the catalysts) is directly involved in this reaction.

#### D. Zinc Chloride for Desulfonation

The ability of an iron solution with additives to desulfonate coal (once successful sulfone formation has occurred) is of interest. Zinc chloride has been used extensively in past coal research for bond-breaking in liquefaction<sup>42,51</sup>. Zinc chloride was used with ferric iron at 200°C under nitrogen in an attempt to desulfonate three sulfones. All runs were for 1 hour at a stir-speed of 300 RPM

with  $\text{ZnCl}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{FeCl}_3$  at 94.4, 4.1, and 1.5 wt-% respectively.

Results of these three runs are given below in Table 29.

Table 29. Results of Desulfonation with Zinc Chloride Melt.

Exp.	Organic	C/H Ratio	C/H Ratio	Oxygen Wt-% Possi-	Oxygen Wt-%
No.	Sulfone	Organic Residue	Sulfone	ble in Residue	in Sulfone
ZN1	DBT·O <sub>2</sub>	17.210	17.873	14.97 Wt-%	14.79 Wt-%
ZN2	DPS·O <sub>2</sub>	14.253	14.299	14.55	14.66
ZN3	DBS·O <sub>2</sub>	-	5.296	-	17.95

No sulfates precipitated from the addition of barium chloride to the aqueous phase after runs ZN1 and ZN2. There may have been some precipitates after run ZN3. There were no ether extractables in the aqueous phase of runs ZN1 and ZN2. From the micro-analysis to determine wt-% possible of oxygen in the residue (column 5 in Table 29) we see that desulfonation did not occur for DBT sulfone or DPS·O<sub>2</sub>. The solid and liquid organic residue from run ZN3 with DBS·O<sub>2</sub> was dissolved in acetone and analyzed by GC/MS (see Appendix D).

The GC/MS analysis showed no di-n-butyl sulfone remaining, but did show butene (either 1-butene, 2-butene, or 2-methyl-1-propene). In addition, there were four smaller peaks. The first small peak was poorly fitted by library files, but was identified as either methylene-propane dinitrile ( $\text{C}_4\text{H}_2\text{N}_2$ ) or a six-carbon ring with formula  $\text{C}_6\text{H}_6$  (benzene or hexadiyne). The second peak was identified as  $\text{C}_6\text{H}_{10}\text{O}$ . Mass spectra were identified as belonging to either 1-cyclopropyl-2-propanone, 3-methyl-4-penten-2-one, or possible 5-hexen-2-one. The third peak was identified as  $\text{C}_6\text{H}_{10}\text{O}$ ,

either 4-methyl-3-penten-2-one, 3-hexen-2-one, or 3-methylene-2-pentanone. The final peak was identified as 4-hydroxy-4-methyl-2-pentanone.

From this analysis, it would appear that the sulfonyl group was completely removed from the di-n-butyl sulfone molecule by the  $\text{ZnCl}_2/\text{Fe}^{+3}$  solution. Zinc chloride may have caused additional cracking of these four-carbon fragments. The iron in solution may then have oxidized these paraffin fragments.

#### IV. SUMMARY AND CONCLUSIONS

The ability of ferric iron, at 150°C in a sulfuric acid-water system, to oxidize coal model compounds varied greatly with the organic compound used. Dibenzothiophene proved to be quite refractory to iron in both nitrogen and oxygen atmospheres, even at long residence times. Transition-metal catalysts had no effect on dibenzothiophene oxidation. Only in one case, under severe oxidation conditions with metavanadate, oxygen, and iron, was there any possibility of oxidation. In this case 40% conversion to sulfone appeared to have occurred in one hour.

Diphenyl sulfide appeared to be oxidized readily. Under nitrogen in iron, 9% oxidation to sulfone could have occurred in one hour. With oxygen 13% conversion could have occurred. Sixty percent oxidation was confirmed at 4 hours, with diphenyl sulfoxide identified as a product. Diphenyl sulfone could also have been a product as well as dibenzothiophene sulfoxide. Catalysts were ineffective in increasing rates.

Experiments with di-n-butyl sulfide under  $N_2$  in  $Fe^{+3}$ /catalyst solutions containing water and sulfuric acid showed that no sulfone formation occurred, but that the C-S bonds were selectively attacked. 1-Butanethiol and 1-butene were identified as products, with  $Fe^{+3}$  reduced to  $Fe^{+2}$  in this process.

In the desulfonation experiments with  $ZnCl_2$  and  $Fe^{+3}$ , dibenzothiophene sulfone and diphenyl sulfone were stable at 200°C for one hour. Experiments with di-n-butyl sulfone under similar conditions showed complete reaction to butenes. During (or after)

the bond breaking, these butenes (or other fragments) appeared to be oxidized, as various propanones and pentenones were seen.

From these results we can conclude that  $\text{Fe}^{+3}$  under mild conditions is selective and effective at oxidizing only the phenyl sulfides. The relatively mild conditions needed to inhibit oxidation of the coal matrix are not severe enough to allow a reasonable rate for dibenzothiophene oxidation. A lengthy residence time of 4 hours was effective in oxidizing roughly 60% of the diphenyl sulfides to various sulfones. The sulfur in dibutyl sulfide did not appear to be selectively oxidized.

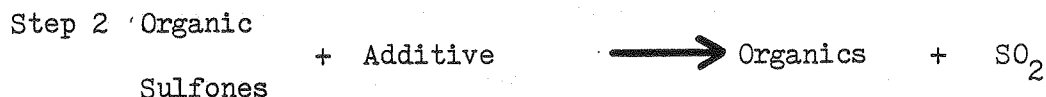
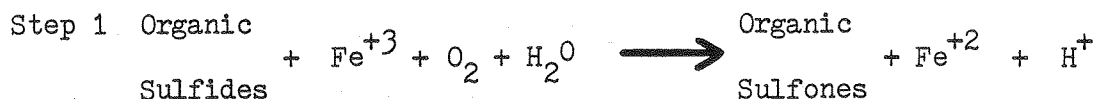
Our method then, would appear to selectively oxidize only the aryl sulfides if applied to coals. These groups comprise only 20% of the total organic sulfur in coal; 8% or less of the total sulfur. The roughly 50% condensed thiophenes in coal would not be affected, while the 20% alkyl groups would apparently not be selectively oxidized, but might be cracked or possibly combusted. Only alkyl sulfones could be attacked after formation in a  $\text{Fe}^{+3}$  system using  $\text{ZnCl}_2$  as a bond breaker.

The C-S bonds in thiophenes appear to resist oxidation under the conditions studied. The C-S bonds in diphenyl sulfides appear to be of the right strength for selective oxidation, while those in dibutyl sulfide are weak enough that they simply break. After conversion to sulfone, C-S bonds in dibenzothiophene and diphenyl sulfone are still strong. Those in dibutyl sulfone are probably even weaker than the sulfide, as they break easily.

## V. RECOMMENDATIONS AND APPLICATIONS

For use in desulfurization of coal, the ferric iron-acid system has been found to completely convert pyrite to iron sulfates, but with as much as 20% oxidation of the coal.<sup>53</sup> This investigation has shown that similar conditions are effective in selectively oxidizing only some of the aryl sulfides. Desulfonation in this system is effective with  $\text{ZnCl}_2$  for only the alkyl sulfones.

For the following process:



The weak steps are steps one and two. We have shown some success in both of these steps using iron and oxygen, as well as a  $\text{ZnCl}_2$ -iron melt. If a suitable additive in the desulfonation (step 2) can be found, this would make this system more attractive, especially if that additive could remove -SH groups. If we could convert the "simple" organics (50% of the total organics) to aryl sulfoxides, sulfones, and alkyl thiols, as demonstrated by iron in acid, an additive (such as  $\text{ZnCl}_2$ ) might remove them under the right conditions. If we could

remove all of the pyrite and the "simple" organics in this manner, the iron-acid leach system could clean possibly three-fourths of the domestic coals.

Obviously this process, as well as pre-combustion oxidation in general, is in need of a major breakthrough. While additives might increase the reaction rates of this system somewhat, the large oxidation of the coal is a very severe price to pay. At present, the iron-acid leach system cannot remove organic sulfur. The system has been shown to have the potential for only some aryl oxidation. If an adequate desulfonation technique could be found, this would only remove an additional 8% of the sulfur in coal, with an unknown added penalty for combustion of coal.

All of the oxidation techniques presently available face severe problems due to non-selective oxidation. Fixation of potentially harmful and/or expensive reactants in the coal (O,N, Cl) are also a difficulty. The availability and environmental impact of using large quantities of water in remote locations, as well as the expense of shipping "wet" coals, add to the bleak outlook for these methods.

If the Meyer's process, or a similar iron-acid leach system, gets a green light for full-scale use in desulfurization, then additional investigation of chemicals which might increase the selectivity of organic sulfur attack is warranted. Otherwise, expensive research seeking to improve the organic removal for this system catalytically is unwarranted. Improvements to existing flue-gas desulfurization methods, or liquefaction and gasification,

may be wiser choices for clean-up efforts due to immediate need for a process which will make clean coal widely available.



APPENDIX A. MICROANALYSIS FOR THE DIBENZOTHIOPHENE  
RUN WITH METAVANADATE.

Microanalysis (C, H, and S) for run 8N (with metavanadate)  
is given below, along with analyses for pure samples of diben-  
zothiophene (DBT) and dibenzothiophene sulfone (DBT·O<sub>2</sub>) for  
comparison.

Organic Residue

from Run 8N

Carbon 73.42 wt-%

Hydrogen 4.24

C/H = 17.316

Sulfur 15.98

93.64 wt-%

Oxygen Possible = 100 - 93.64 = 6.36 wt-%

(By Difference)

Dibenzothiophene Sample

<u>Theoretical</u>	<u>Actual</u>
C 78.222 wt-%	C 78.42 wt-%
H 4.376	H 4.46
S 17.401	S 17.34
<u>100.0 wt-%</u>	<u>100.22 wt-%</u>
C/H = 17.874	C/H = 17.583

Dibenzothiophene Sulfone Sample

<u>Theoretical</u>	<u>Actual</u>
C 66.648 wt-%	C 67.20 wt-%
H 3.729	H 3.99
S 14.827	S 13.84
O 14.796	<u>85.03 wt-%</u>
<u>100.0 wt-%</u>	Oxygen Possible =
C/H = 17.874	100 - 85.03 =
	14.97 wt-%
	C/H = 16.842

APPENDIX B. MICROANALYSIS AND GC/MS DETAIL FOR  
DIPHENYL SULFIDE RUNS.

Microanalysis results for the organic material from diphenyl sulfide runs 8I and 8J are given below. Samples of unreacted diphenyl sulfide and diphenyl sulfone are given for comparison.

Organic Residue  
from Run 8I

C	74.92 wt-%
H	5.43
S	17.46
<hr/>	
	97.81

Oxygen

Possible

= 100 - 97.81

= 2.19 wt-%

C/H = 13.797

Organic Residue  
from Run 8J

C	70.95 wt-%
H	5.45
S	14.84
<hr/>	
	91.24

Oxygen

Possible

= 100 - 91.24

= 8.76 wt-%

C/H = 13.018

Diphenyl Sulfide Sample

<u>Theoretical</u>	<u>Actual</u>
C 77.38 wt-%	C 77.43 wt-%
H 5.41	H 5.50
S 17.21	S 16.94
<hr/>	<hr/>
100.0 wt-%	99.87 wt-%
C/H = 14.300	C/H = 14.078

Diphenyl Sulfone Sample

<u>Theoretical</u>	<u>Actual</u>
C 66.03 wt-%	C 66.11 wt-%
H 4.62	H 4.66
S 14.69	S 14.50
O 14.66	<hr/>
<hr/>	85.27
100.0 wt-%	Oxygen
C/H = 14.300	Possible
	= 100 - 85.27
	= 14.73
	C/H = 14.187

Results from the GC/MS for run 8J are given below. "Fit" is the match of the sample spectra to those in the computer library, "Refit" is the match of the suggested compound's spectra to those of the unknown (1000 is a perfect match).

Suggested Compounds			
	<u>from Library Search</u>	<u>Fit</u>	<u>Refit</u>
Peak 1	Diphenyl Sulfide (C <sub>12</sub> H <sub>10</sub> S)	984	893
2	Dibenzothiophene (DBT) (C <sub>12</sub> H <sub>8</sub> S)	922	535
or	DBT Sulfoxide (C <sub>12</sub> H <sub>8</sub> SO)	798	530
3	Diphenyl Sulfoxide (C <sub>12</sub> H <sub>10</sub> SO)	985	839
or	Ethenyl-sulfonyl-benzene (C <sub>8</sub> H <sub>8</sub> SO <sub>2</sub> )	735	232
4	Diphenyl Sulfone (C <sub>12</sub> H <sub>10</sub> SO <sub>2</sub> )	580	220

APPENDIX C. GC/MS DETAIL FOR DI-n-BUTYL SULFIDE RUN

The detail of GC/MS analysis for run 8L(C) is given below. Four compounds were identified in the organic residue after the run. Ether was used as a solvent. "Fit" is the match of sample spectra for a peak with those in the library files (1000 is maximum overlap), "Refit" is the corresponding comparison of selected library spectra with those of the unknown.

Suggested Compounds			
	<u>from Library Search</u>	<u>Fit</u>	<u>Refit</u>
Peak 1	Butene	-	-
2	Ether (C <sub>4</sub> H <sub>10</sub> O)	980	974
3	1-Butanethiol (C <sub>4</sub> H <sub>10</sub> S)	846	809
4	Di-n-Butyl Sulfide (C <sub>8</sub> H <sub>18</sub> S)	972	926

APPENDIX D. GC/MS DETAIL FOR  $\text{ZNCL}_2$  DESULFONATION OF  
DI-n-BUTYL SULFONE.

The detail for GC/MS analysis for run ZN3 is given below.  
Six peaks were identified. Acetone was used as a solvent. "Fit"  
is a match to the spectra in library files (1000 is a maximum),  
"Refit" is a match of identified library compound spectra with  
the unknown.

Suggested Compounds			
	<u>from Library Search</u>	<u>Fit</u>	<u>Refit</u>
Peak 1	Acetone	-	-
2	1-Butene ( $\text{C}_4\text{H}_8$ )	947	327
3	Methylene-propane- dinitrile ( $\text{C}_4\text{H}_2\text{N}_2$ )	902	154
or	Benzene ( $\text{C}_6\text{H}_6$ )	837	157
4	1-Cyclopropyl-2-pro- panone ( $\text{C}_6\text{H}_{10}\text{O}$ )	915	881
or	3-Methyl-4-penten-2- one ( $\text{C}_6\text{H}_{10}\text{O}$ )	923	813
or	5-hexen-2-one ( $\text{C}_6\text{H}_{10}\text{O}$ )	854	833
5	4-methyl-3-penten-2-one ( $\text{C}_6\text{H}_{10}\text{O}$ )	965	933
or	3-hexen-2-one ( $\text{C}_6\text{H}_{10}\text{O}$ )	955	918
or	3-methylene-2-pentanone ( $\text{C}_6\text{H}_{10}\text{O}$ )	932	914

Suggested Compounds			
	<u>from Library Search</u>	<u>Fit</u>	<u>Refit</u>
Peak 6	4-hydroxy-4-methyl- 2-pentanone (C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> )	961	851

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